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RAMAN SPECTRA IN ORGANIC CHEMISTRY

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I. INTRODUCTION

Raman spectra in inorganic chemistry have been reviewed in a previous article (311). In addition to a summary of most of the data accumulated by 1934, this review included in some detail the theoretical background, such as the conditions which give rise to the Raman effect, selection rules, its relation to infra-red absorption, and the magnitude, intensity, and polarization of Raman shifts. It would serve no useful purpose, therefore, in this survey of Raman spectra in organic chemistry to repeat in detail all the theoretical aspects of the subject, as these are equally applicable to the inorganic and organic fields. Furthermore, while theoretical concepts have been perfected during the past two years, there has been no fundamental alteration in them. In order to reduce the wide scope of this review as much as possible, reference to the inorganic spectra will be avoided. It cannot be overemphasized, however, that the principles treated and the information obtained are nearly identical in both cases.

The Raman effect of considerably over a thousand organic compounds has been investigated. It is the purpose here to discuss the spectra of these compounds in somewhat general terms, rather than to record every individual Raman shift for all compounds. The shifts attributed to the types of linkage in each class of compounds, however, will be discussed. In order that reference to original work may be made conveniently, the attempt has been made to include in the bibliography all publications giving original data on organic compounds since the discovery of the Raman effect by Sir. C. V. Raman in 1928. Each compound studied is listed alphabetically by name and according to its empirical formula, with the appropriate literature citations. An additional bibliography of articles on inorganic Raman spectra which have appeared since the earlier compilation (311) is included.

The particular efficacy of the Raman effect lies in the fact that it is a physical method causing no chemical change and is roughly independent of the state of aggregation of the material to be examined and its chemical composition. From it can be obtained considerable information regarding the internal and external characteristics of the molecule. The strength of the bonds between the atoms in their normal state and the frequency and amplitude of atomic vibration can be calculated. In some cases the spacial configuration and the anisotropy of the molecule may be determined. From this information the specific heats, relative heats of dissociation, and the possible heats of fusion of pure organic compounds may be estimated. In addition, it may serve as a method of identification of compounds in mixtures and in the determination of complex molecular structure. The activity in this field, then, is not surprising. Its progress has paralleled that of other scientific discoveries: first, the correlation of an experimental observation with theory and other phenomena—in this case spectroscopic; second, an accumulation of qualitative data; and finally, a development in a more quantitative fashion. Raman spectra have attained, at least partially, the final status.

II. DEFINITION OF TERMS

The Raman lines or Raman shifts are generally given in terms of wave numbers or the number of vibrations per centimeter. Any spectroscopic line may be defined by $\lambda\nu = 3 \times 10^{18}$, where λ is the wave length in Ångström units (A.U.), the digits represent the velocity of light in A.U., and ν the frequency, or $\lambda\bar{\nu} = 10^8$ where $\bar{\nu}$ is defined in wave numbers per centimeter. Since the Raman lines are the differences between spectroscopic lines it is more or less customary to employ $\Delta\bar{\nu}$ to express this. The Raman shifts will be given in wave numbers per centimeter, that is, $\Delta\bar{\nu} = 500$ cm.$^{-1}$, for example, or more simply, $\Delta\bar{\nu}$ 500. The relative intensities, when given, are in parentheses and follow the Raman shift numbers, for example, $\Delta\bar{\nu}$ 500 (7); they are on a basis of ten.

Other terms used are as follows: $\bar{\mu}$ represents the reduced mass, that is,

$$\frac{1}{\bar{\mu}} = \frac{1}{M} + \frac{1}{m}$$

where M and m represent the weights in a vibrating system. F is the elastic restoring force, or the force per unit displacement expressed in dynes per centimeter. d is the deformation force constant in dynes per centimeter. h is Planck's constant, 6.54×10^{-27} erg seconds. N is Avogadro's number, 6.06×10^{23}. ρ is the degree of depolarization. k is the Boltzmann constant, 1.37×10^{-16} ergs per degree.

III. ORIGIN OF RAMAN SPECTRA

Raman spectra owe their origin to the interaction of a light quantum ($h\nu$) and a molecule. This is not unlike an inelastic collision between two molecules. In this case it is conceivable that one molecule will be deflected with less energy after the impact and the other molecule will absorb some of the energy as kinetic or potential energy. In the Raman effect each mode of oscillation in the molecule which interacts with the light quantum results in an absorption of energy from this quantum and its consequent rescattering with less than its initial energy. This rescattered radiation may be recorded photographically by means of a spectrograph. The light quantum giving rise to this scattering is generally obtained from the emission spectrum of mercury or helium and is similarly recorded. This source of monochromatic light is generally termed the exciting radiation. The scattered radiations of less energy than the

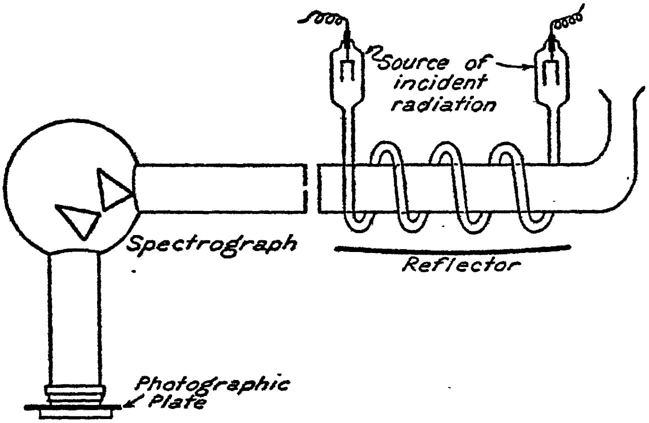


FIG. 1. Experimental arrangement for recording Raman spectra

exciting frequency are the Raman frequency shifts or Raman lines. If a molecule in a vibrational or rotational level above the ground level interacts with a quantum of light, Raman lines of higher frequency than the exciting radiation may be emitted. These are anti-Stokes lines and are identical with the lower frequency shifts, but have intensities proportional to the population of the molecules in the upper levels. Each exciting source will give rise to a complete series of Raman lines. A commonly used excitation line is the mercury violet line at 4047 A.U., the Raman shifts appearing in the spectrum from 4047 A.U. to the blue-green region near 4800, depending on the compound irradiated. A schematic diagram of the experimental arrangement for recording Raman spectra is given in figure 1. Since each type of vibration or rotation gives rise to a Raman line, in a diatomic molecule only one vibrational Raman line is probable. These vibrations are analogous to a simple mechanical system consisting of two masses held together with a spring. The frequency at which they vibrate is represented by the simple equation

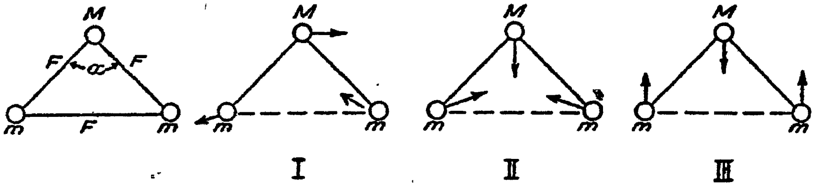


FIG. 2. The motions of a non-linear triatomic model

$$\nu = \frac{1}{2\pi} \sqrt{F/m} \tag{1}$$

where ν represents the mechanical frequency of vibration, m the mass of vibrating components, and F the force per unit displacement exerted between them. In an atomic system with ν expressed in wave numbers per centimeter and the masses by the relative atomic weights, this becomes

$$\Delta\bar{\nu} = 4.125 \sqrt{\frac{F}{m}} \tag{2}$$

from which either F or $\Delta\bar{\nu}$ may be calculated.

A system of three atoms of type AX_2 may exist in linear or non-linear forms. The motions of a non-linear model are illustrated in figure 2. Here the asymmetrical oscillation is indicated by I, the symmetrical by II, and the deformation motion by III.

For the linear model the Raman shift $\Delta\tilde{\nu}_1$ may be calculated if $\Delta\tilde{\nu}_2$ is known, by the relation,

$$\Delta\tilde{\nu}_1 = \Delta\tilde{\nu}_2 \sqrt{\frac{M + 2m}{M}} \tag{3}$$

and similarly for a model where spacial arrangement is in the form of an equilateral triangle of type X_3,

$$\frac{\Delta\tilde{\nu}_1}{\Delta\tilde{\nu}_2} = \sqrt{\frac{3F/m}{3F/2m}} = \sqrt{2} \tag{4}$$

The valence angle in non-linear simple diatomic models can be roughly approximated from the equation

$$\frac{\Delta\tilde{\nu}_1}{\Delta\tilde{\nu}_2} = \sqrt{\frac{M + 2m\sin^2\alpha}{M + 2m\cos^2\alpha}} \tag{5}$$

The greatest amplitude of vibration of the masses is given by

$$\bar{a} = \sqrt{\frac{2hN}{2\pi^2 c}} \cdot \sqrt{\frac{1}{\mu\Delta\tilde{\nu}}} \tag{6}$$

The frequencies calculated from these formulas are in many cases in reasonable accord with the experimental observations. Conversely, the molecular configuration necessary to give rise to the correct number and distribution of Raman lines can be determined. The mechanical models of Andrews and his coworkers (16, 331, 587) and of Trenkler (599, 600), which simulate the vibrations of atoms in molecules, give rise to frequencies of vibrations in fair agreement, in some cases, with observed Raman shifts. Any lack of agreement in either case is due primarily to over-simplification either mathematically or mechanically.

The usefulness of mechanical models is restricted largely to the study of certain relatively simple and stable types of vibration. Nevertheless, they indicate the realistic nature of the Raman effect and have a useful purpose. The valence force systems and central force systems of calculating the vibrational frequencies in more complicated molecules have been sufficiently fruitful (particularly the former) to indicate the general applicability of the more or less mechanical conception. Recently Wilson (648, 649, 650) has treated the problem analytically by means of the group theory, with calculable results compatible with the observed frequencies. A Raman spectrum is not, therefore, a matter of prestidigitation but has a sound statistical and theoretical basis. Furthermore, a reasonable extrapolation can be made in its application which carries its usefulness far beyond a spectroscopic phenomenon. Before proceeding further with this phase of Raman spectra it should be emphasized that while these applications are treated more or less as a static manifestation they are in reality dynamic. All chemical linkages actually are not entirely fixed but may resonate between themselves. In discussing the shifts for particular organic compounds no attempt has been made to give a weighted value, but rather typical results. Reference should be made to the index of compounds for more detailed data. It is not possible to cite in the text all the contributions made by the large number of workers in this field. Those thus cited have been chosen for context or to illustrate different methods of approach.

IV. THE RAMAN SPECTRA OF ORGANIC COMPOUNDS

A. The Raman spectra of saturated aliphatic hydrocarbons

It has already been indicated that the magnitudes of Raman shifts are a function of the force exerted between the atoms in a molecule, the type of motion, and the relative masses of the atoms. Andrews (11) early noted that the force constant calculated from equation 2 was relatively constant for a single homopolar linkage, namely, approximately 5×10^5 dynes per centimeter, and nearly double and treble this value for double or triple bonds. This is indicated in table 1.

TABLE 1

Valence forces (F) for different types of linkage

LINKAGE	$F \times 10^{-5}$ DYNES CM.$^{-1}$	LINKAGE	$F \times 10^{-5}$ DYNES CM.$^{-1}$
H—H	5.38	N—H	6.39
C—H	5.02	O—H	6.72
C—C	4.40	C—N	4.53
C—O	5.05		
C=C	11.0	C≡C	14.82
C=O	11.7	C≡N	19.23
O=O	11.4	C≡O	18.83

As the masses of the vibrating components decrease, the Raman shifts will increase. It is not surprising, therefore, that the shifts corresponding to the linear oscillation of the C—H are of large magnitude. These vary from 2800 to 3400 wave numbers per centimeter. This rather wide scale is due to some variation in the force constant as a function of constitution, as will be seen later. In table 2 are given some of the shifts for C—H observed by Bhagavantam (47) in the simpler hydrocarbons, and in figure 3 a reproduction of their Raman spectra as recorded on a photographic plate.

Methane is a molecule of the type AX_4 and has a tetrahedral structure, consequently there should exist several frequencies describing the atomic motions. Not all of these are present either as Raman lines or infra-red absorption. In order to have infra-red absorption by a molecule there must be a change in moment arising from an atomic oscillation. Infra-red absorption bands may be absent when a given transition from one energy level to another is forbidden. Raman lines may be excited even if a transition between two characteristic levels is forbidden, if a common third discrete level exists to which a transition is possible from any two levels. In methane there appear $\Delta\bar{\nu}$ 1304 and $\Delta\bar{\nu}$ 3019 as infra-red absorption, and these are attributed to the unsymmetrical motion of the carbon atom. The latter frequency appears in Raman spectra as a weak line.

TABLE 2

The hydrogen to carbon oscillations of some simple hydrocarbons

HYDROCARBON	HYDROGEN OSCILLATIONS IN $\Delta\bar{\nu}$										
Methane.							2918 (10)			3018 (2b)	3066 (1)
Ethane.							2900 (9)	2955 (10)			
Propane.	1453 (4)		2728 (3)	2767 (1)	2874 (10)	2903 (3)	2920 (5)	2948 (3)	2968 (3)		
Butane.	1453 (10b)	2665 (1)	2706 (1)	2736 (2)	2864 (4)	2879 (8)	2910 (3)	2938 (6)	2964 (3)		
Isobutane.....	1453 (10b)	2624 (1)	2720 (4)	2777 (2)	2870 (10)	2892 (2)	2910 (3)	2936 (3)	2962 (8)		

On the other hand $\Delta\bar{\nu}$ 2918 is the inactive oscillation forbidden in infra-red absorption but strong in Raman spectra and probably arising from the symmetrical motion of the hydrogen atoms in the expansion and contraction of the tetrahedron. In liquid methane Daure (194) and McLennan, Smith, and Wilhelm (424) have observed additional lines. It is not possible to obtain all the fundamental oscillations of methane as Raman lines.

While one strong line is characteristic of the linear $C \leftrightarrow H$ oscillation in methane, in ethane there are two strong lines, $\Delta\bar{\nu}$ 2900 and 2955. This multiplicity of lines increases with the complexity of the molecules up to butane, after which there is no marked change. The appearance of these new lines is attributed to the perturbing influence of valence forces. The linear oscillation of the hydrogen attached to the central carbon atom in propane is obviously going to be affected by the adjacent methyl

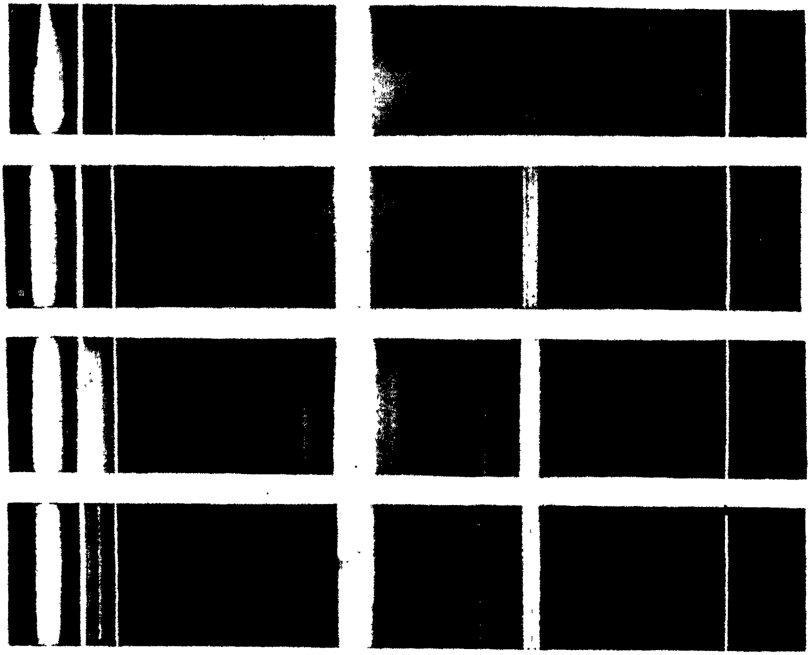


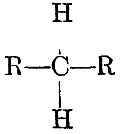
FIG. 3. The Raman spectra of some simple hydrocarbons as recorded on photographic plates (after Bhagavantam)

TABLE 3

Raman shifts for C—H *vibrations*

LINKAGE	$\Delta\bar{\nu}$	LINKAGE	$\Delta\bar{\nu}$
C—H (aliphatic)	2918	$\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}C}$	2970
C—H (aromatic)	3054		
$\mathrm{C{-}\overset{H}{\underset{H}{C}}{-}H}$	2930 2862	$\mathrm{\overset{H}{\underset{H}{C}}}$ (transverse)	1450

groups. Petrikaln (497), Andrews (11), Dadieu and Kohlrausch (175), and High (316) conclude that the approximate assignment of frequencies for C↔H is as shown in table 3. The shift at $\Delta\bar{\nu}$ 1450 appearing in propane arises from the transverse oscillation of the hydrogen in respect to carbon and appears in all organic compounds having the



$$R-\overset{H}{\underset{H}{C}}-R$$

group. The force constant for this type of vibration is approximately one-fifth that of the linear oscillation. All these frequencies are absent in carbon tetrachloride and similar compounds containing no hydrogen. It is to be noted that even in methane there may be combination frequencies which have not been mentioned. For the higher members of the homologous series there are "inner vibrations" roughly independent of the rest of the molecule and "outer vibrations" which depend on the mass of the vibrating aggregates.

TABLE 4

The carbon to carbon oscillations of some simple hydrocarbons

HYDROCARBON	CARBON OSCILLATIONS IN $\Delta\bar{\nu}$									
Methane										
Ethane				993						
				(5)						
Propane		377		867			1055		1155	
		(2)		(10)			(2b)		(2)	
Butane	320	430	793	834	960	983	1060	1067	1146	1303
	(0)	(6)	(4)	(10)	(3)	(3)	(6)	(0)	(4)	(3b)
Isobutane	372	436		796	967				1177	1355
	(4b)	(2b)		(10)	(5b)				(5b)	(4b)

The carbon to carbon linkages in these compounds present a much more complex problem. In ethane appears the shift $\Delta\bar{\nu}$ 993, corresponding to the symmetrical C↔C vibration. This decreases to $\Delta\bar{\nu}$ 867 in propane, to $\Delta\bar{\nu}$ 834 in butane, and thereafter becomes relatively constant. The transverse shifts due to the bending moment for the C—C linkage appear below $\Delta\bar{\nu}$ 600, decreasing slightly with each added CH_2 increment. The total number of lines which occur will depend on the molecular configuration and the interaction of the valence forces. Those which lie between $\Delta\bar{\nu}$ 800 and $\Delta\bar{\nu}$ 1100 are generally attributed to the carbon to carbon oscillations, although Simons (562) would extend this in some cases to as high as $\Delta\bar{\nu}$ 1400. Between $\Delta\bar{\nu}$ 1100 and $\Delta\bar{\nu}$ 1460 are the deformation oscil-

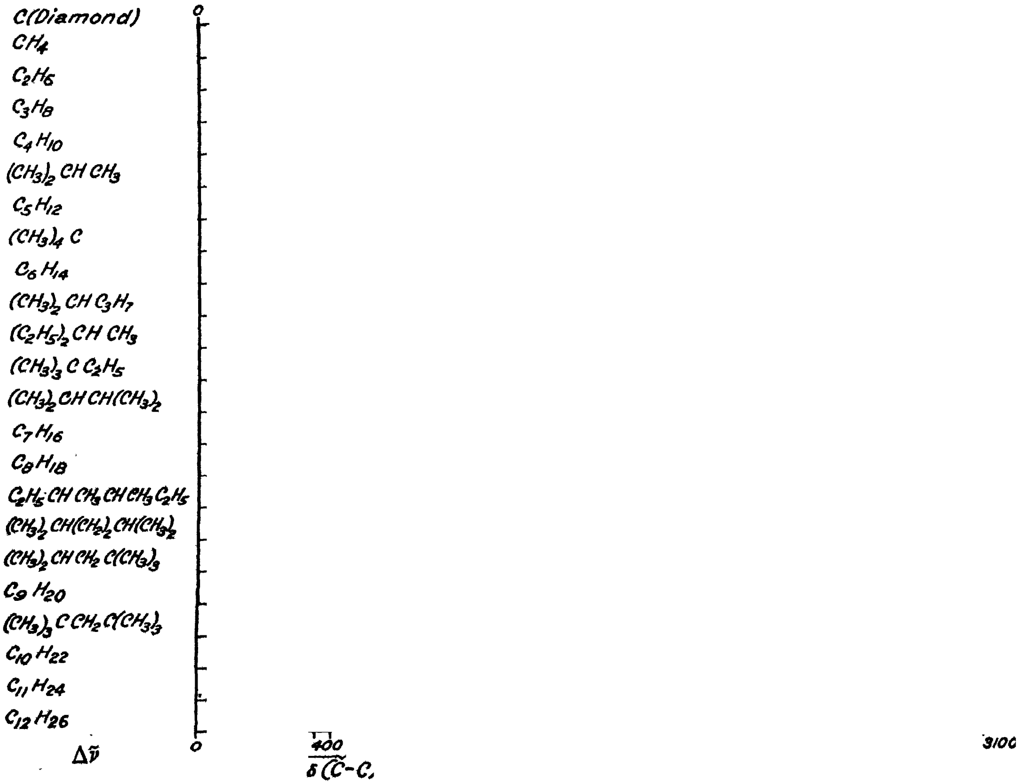


FIG. 4. Comparison spectra of saturated aliphatic hydrocarbons. (In order to have a form system of presentation in the figures, intensity estimates of other authors have been tr lated into the height of vertical lines.)

lations of C—H and finally, beginning at approximately $\Delta\bar{\nu}$ 2700, occur the symmetrical C—H oscillations. The C—C Raman shifts for the simpler hydrocarbons (49) are given in table 4. That the distribution of the lower carbon shifts is influenced by the centralization of the molecular groups is evidenced by the change in spectra proceeding from normal butane to tetramethylmethane or in the isomeric hexanes studied by Andant, Lambert, and Lecomte (9). Kohlrausch (341) suggests a constitutional influence in *n*-butane attributed to a zigzag or -shaped chain. In figure 4 are given the comparison spectra of most of the saturated aliphatic hydrocarbons which demonstrate the differentiating characteristic shifts.

The isomeric paraffins have been considered in detail by Tetetleni (588), Kohlrausch and Köppl (347, 349), and Dadieu, Pongratz, and Kohlrausch (191). According to Tetetleni the isomeric derivatives of the aliphatic compounds are richer in Raman lines and are more similar to each other than the cyclic compounds. Kohlrausch and his coworkers believe the chain frequency is slightly higher in the branched than in the normal chain compounds. The central force system fails to describe all the results, and the valence force system is only moderately accurate. As has been indicated, there is some decrease in the frequency shift which corresponds to the linear oscillation of the end vibrating group against the rest of the chain in the isomeric paraffins and possibly some differences in hydrogen frequencies depending on the type of branching. Individually there are considerable differences between the various isomers, as for example in the hexanes whose spectra are given in figure 4.

In interpreting these comparison spectra it must be borne in mind that differences in the spectra presented may not be real but may be due to the experimental conditions employed by several observers. A short exposure, designed to record only the strong lines in one compound, would make its spectrum apparently more simple than a much less complex compound exposed a longer time. There are undoubtedly other hydrogen lines in the $\Delta\bar{\nu}$ 3000 region for the hexanes, for example, which were not recorded. By comparing intensities of low wave number shifts and common shifts, both strong and weak, it is usually possible to distinguish actual spectral differences from fictitious ones. There is, of course, no difficulty when the spectra of the compounds are taken under reasonably comparable circumstances.

B. *The Raman spectra of halogen derivatives of saturated aliphatic hydrocarbons*

In a diatomic molecule of the type HCl, HBr, or HI one would expect a progressive diminution of the Raman shift with increased mass of the

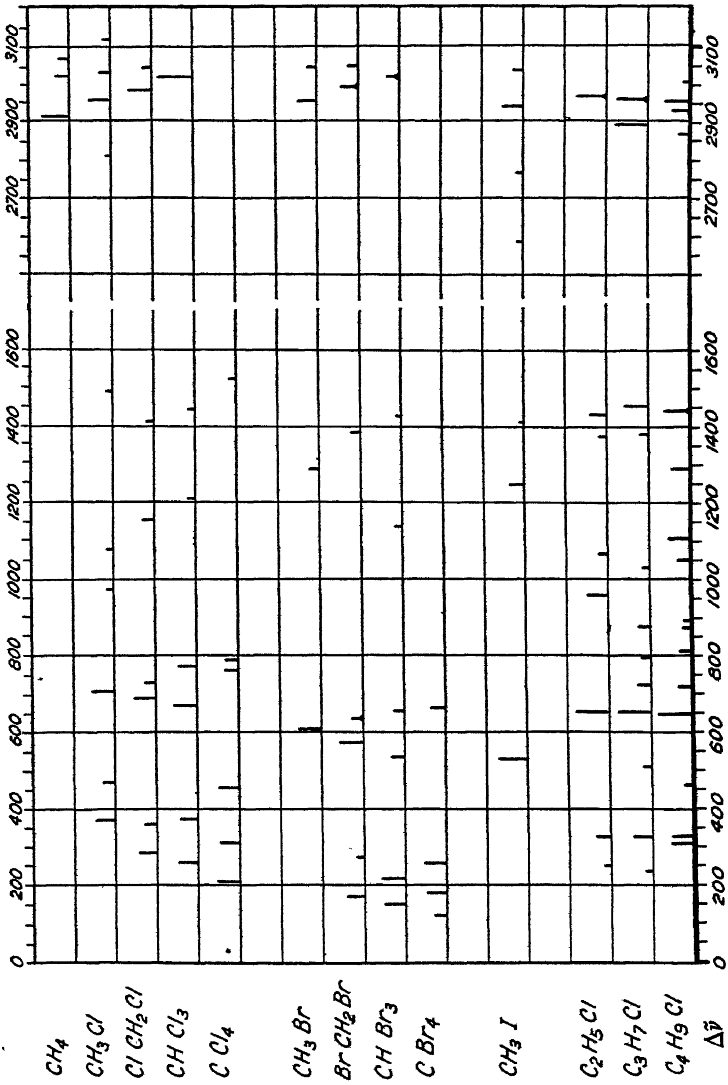


Fig. 5. Comparison spectra of some halogenated aliphatic hydrocarbons

anion. This is realized experimentally, the observed shifts being $\Delta\bar{\nu}$ 2880, 2558, and 2233, respectively. Similarly in halogen-substituted methanes there is a corresponding progressive decrease in the values for the symmetrical oscillation $X \leftrightarrow CH_3$, concomitant with a change in the vibrational quantum number of ±1. For methyl chloride, bromide, and iodide the decreases are $\Delta\bar{\nu}$ 710, 600, and 530, and in ethyl chloride, bromide, and iodide, $\Delta\bar{\nu}$ 654, 566, and 497. The change in masses alone is insufficient to explain this decrease. Harkins and Bowers (295) calculate the force constants which will balance the equation for the halogen derivatives of methane as being respectively 3.02, 2.6, and 2.17×10^5 dynes $cm.^{-1}$ and hence much lower than the average value of 5×10^5 dynes $cm.^{-1}$ found for ethane. Furthermore, the decrease in value from bromine to iodine is only slightly greater than 50 per cent of the decrease between chlorine and bromine. The results are further substantiated by West and Farnsworth (642), who observe that increasing the length of the chain beyond three carbon atoms causes no further decrease in the longitudinal Raman shift in a homologous series of monohalogen derivatives. Apparently the effective vibrating mass of carbon and hydrogen is 17, or slightly greater than one CH_2 group, regardless of the length of the chain. If, however, branching occurs near to the halogen atom the shift is reduced by approximately 30 wave numbers.

In addition to the wave numbers cited there occurs another series of shifts of lower value, possibly attributable to the transverse motion of the C—X linkage. These are for R—Cl $\Delta\bar{\nu}$ 333, R—Br $\Delta\bar{\nu}$ 280, and R—I $\Delta\bar{\nu}$ 260, although the last item is confined to a few observations (175). The changes are depicted graphically in figure 5. The absence of shifts in methyl bromide below $\Delta\bar{\nu}$ 600 is without significance. Practically all those occurring below $\Delta\bar{\nu}$ 800 are attributed to the halogen substitution. By comparing figures 4 and 5 it will be seen that the presence of a halogen derivative could be detected in a hydrocarbon mixture by means of these characteristic shifts. The effect of increasing halogen substitution in a hydrocarbon on the C—H oscillations is to augment progressively the frequency of oscillation indicative, in this case, of greater bond strength, as the increased mass would diminish rather than enlarge this frequency. On the other hand, when substitution takes place on the β-carbon atom relative to the methyl group, there is little or no effect on the linear hydrogen vibration.

Cleetin and Dufford (129) have advanced the hypothesis that the shifts observed are fundamental and combination frequencies. Assuming an unobserved fundamental of $\Delta\bar{\nu}$ 90, then the spectrum of methyl iodide is accounted for as follows:

	observed	*calculated*
$\Delta\tilde{\nu}$	534	ν_3
	2859	$\nu_4 - 4\nu_1$
	2771	$\nu_4 - 2\nu_1$
	2946	ν_4
	3036	$\nu_4 + \nu_1$

where $\nu_1\ \nu_2 \ldots$ is somewhat inconsistently but universally used with reference to fundamentals and is equivalent to $\Delta\tilde{\nu}$. It will be used here in this manner. The results are in fair agreement in this and other cases. As these authors themselves point out, however, calculated results obtained with the *ad hoc* assumption of one or more fundamental frequencies are to be accepted with caution. Nevertheless, there is no doubt that combination frequencies may exist in Raman spectra.

Adel and Barker (1) have reviewed Bennet and Meyers' and Dennison's analyses of the vibrations of the methyl monohalides based on infra-red absorption.

By applying the wave function

$$\Psi_0 = \Psi^{\nu_1}_{(\sigma)}\Psi^{\nu_4 l}_{(\rho)}e^{\pm il\varphi}$$

where ν_1, ν_4 and l are the quantum numbers of vibration and $\Psi^{\nu_1}_{(\sigma)}$ and $\Psi^{\nu_4}_{(\rho)}$ are respectively the Hermitian orthogonal function with argument σ and the associated Laguerre orthogonal function with argument ρ^2 to determine the zero$^{\text{th}}$ order solution of the zero$^{\text{th}}$ order system of vibration, they conclude that there is an interaction between vibrational levels at $\Delta\tilde{\nu}$ 1460 and $\Delta\tilde{\nu}$ 2955 representing the fundamentals ν_4, ν_1, the former combining to $2\nu_4$ which interacts with ν_1, producing a resonance splitting of energy levels which will account for the C—H lines.

C. The Raman spectra of aliphatic alcohols

From the point of view of Raman spectra the delineation of the structures of the alcohols is one of its less fruitful applications. This is primarily because the force constant for C—OH is very much the same as that of C—C, and the relative mass of the OH group differs from that of a CH_3 group by only two units. There have been numerous attempts to assign specific Raman frequencies to types of vibrations in the alcohols. In the simpler cases this is undoubtedly a correct procedure. In the more complicated molecules, however, it is exceedingly difficult to distinguish between the vibrations of a hydrocarbon and those of a corresponding alcohol. It is of course obvious that the frequency at $\Delta\tilde{\nu}$ 1030 which appears in methyl alcohol is analogous to $\Delta\tilde{\nu}$ 993 in ethane and is attribut-

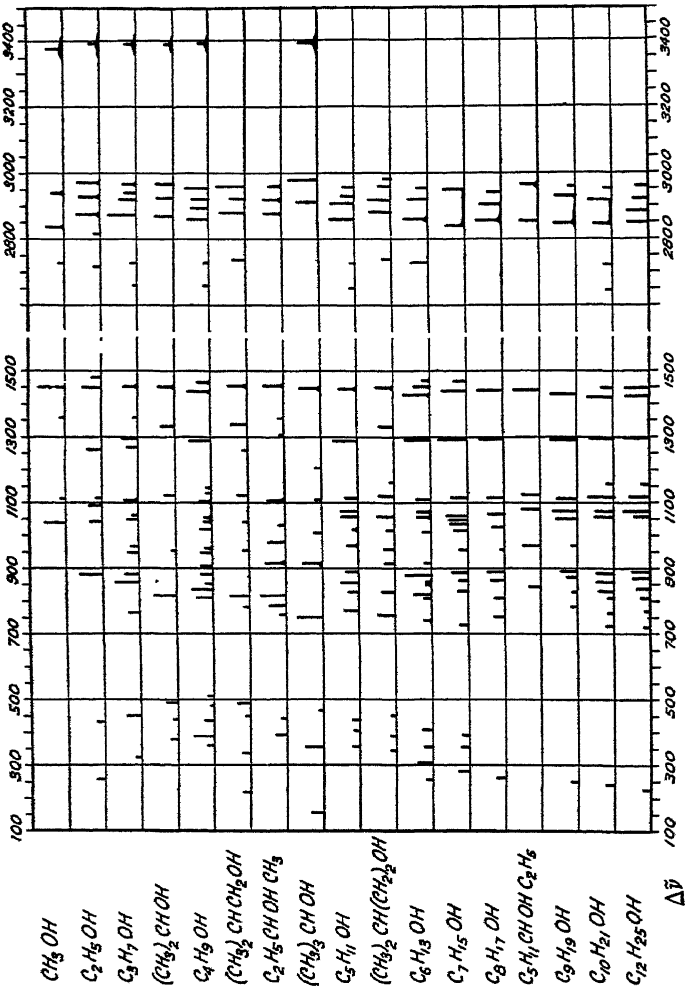


FIG. 6. Comp ;t aliphatic alcohol
]

able to the linear oscillation of the HO against the CH_3 group. Furthermore, as with the first members of the hydrocarbon series, there is a decrease in the magnitude of this oscillation with increased chain length. From ethyl to butyl alcohol inclusive this displacement has the values $\Delta\tilde{\nu}$ 885, 856, and 825, which is in reasonable accord with the change in vibration arising from the increased mass of one of the vibrating components as calculated by Trumpy (602).

With some alcohols there appears a very broad band of a width from 80 to 500 wave numbers, which can be resolved into several components; this is undoubtedly caused by the H↔O oscillation. This generally occurs with a maximum near $\Delta\tilde{\nu}$ 3400. Unfortunately, however, this can only be detected in less than half of the alcohols studied. The infra-red counterpart of this shift, according to Wulf, is a sharp band. In figure 6 are given the spectra obtained from a series of aliphatic alcohols, mainly based on the work of Collins (133), Wood and Collins (661), Nevgi and Jatkar (471), and Kohlrausch (336). The shifts near $\Delta\tilde{\nu}$ 3400 are those observed by Médard (427).

Venkateswaran and Bhagavantam (626) attribute the shifts occurring near $\Delta\tilde{\nu}$ 1050, 1240, and 1360 to the C—OH group. The shifts between $\Delta\tilde{\nu}$ 1000 and 1250 are so numerous, and they are so close to those appearing in the normal hydrocarbons that is is impossible to say for a certainty that they owe their origins to the OH group. The shifts near $\Delta\tilde{\nu}$ 1450 occur likewise in the hydrocarbons, and are probably exclusively due to the transverse hydrogen vibration. The shifts near $\Delta\tilde{\nu}$ 1360 are present in only a few alcohols and those near $\Delta\tilde{\nu}$ 1300 in most hydrocarbons. It is noteworthy, however, that this latter shift is undoubtedly displaced toward a higher frequency in the isomeric alcohols. Furthermore, the spectra from the isomers are apparently more simple than those from the straight chain compounds. After the molecule reaches a length corresponding to nine carbon atoms there is very little change in the spectra (31).

Nevgi and Jatkar (471) attribute the frequencies from $\Delta\tilde{\nu}$ 2880 to $\Delta\tilde{\nu}$ 2960 to the longitudinal hydrogen vibration, $\Delta\tilde{\nu}$ 2880 arising from the α-CH, $\Delta\tilde{\nu}$ 2930 from the β-CH, and $\Delta\tilde{\nu}$ 2970 from the end CH which is the most free to vibrate. The assignment of $\Delta\tilde{\nu}$ 2880 to the α-CH is supported by its absence in tertiary butyl alcohol, but this conclusion is annulled by its presence in tertiary amyl alcohol. The $\Delta\tilde{\nu}$ 2747 occurring in isobutyl and isoamyl alcohols was attributed by them to the linear oscillation of a hydrogen atom in juxtaposition to two methyl groups. This view seems to be untenable, as this frequency shift occurs in several of the other alcohols which contain no substituted methyl groups.

Collins (133) has systematically investigated the lower frequency shifts in a series of octanols whose structures differ only in the relative position of a methyl and hydroxyl group. When the compound has methyl groups only at the end of the molecule $\Delta\bar{\nu}$ 1300 is sharp, but if the molecule is branched this shift becomes either a doublet or broad. The inference is that the branched methyl groups have a slightly different frequency which accounts for this change. However, when the side-chain methyl group is attached to the same carbon atom as the hydroxyl group, as in 2-methyl-2-heptanol, 3-methyl-3-heptanol, and 4-methyl-4-heptanol, the line at $\Delta\bar{\nu}$ 1300 remains sharp and a new line appears at $\Delta\bar{\nu}$ 755. The origin of the Raman line between $\Delta\bar{\nu}$ 800 and $\Delta\bar{\nu}$ 1000 is ascribed to the vibration of the hydroxyl group against the chains and the apparent doubling of the lines between $\Delta\bar{\nu}$ 1000 and $\Delta\bar{\nu}$ 1200 to the influence of the hydroxyl or methyl group in the side chain. Neither of these conclusions is completely tenable, as a comparison of figure 4 with figure 7 will demonstrate.

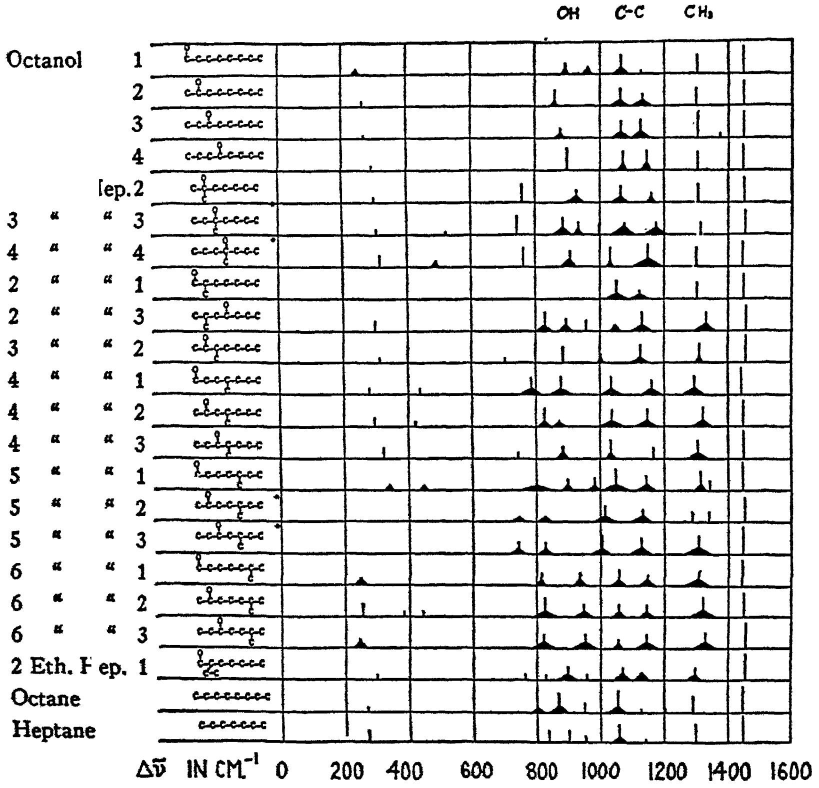


FIG. 7. Comparison spectra of nineteen octanols (after Collins)

Assuming a valence angle of $\theta = 108°$ obtained from x-ray measurements and a force constant of 4.3×10^5 dynes per centimeter between the carbon atoms in a long chain, the $\Delta\bar{\nu}$ calculated from the equation

$$\Delta\bar{\nu} = \frac{1}{2}\left(\frac{2F \cos \theta/2}{\bar{\mu}}\right)^{1/2}$$

is 1075 for the inner C—C vibration.

The most comprehensive investigation of an alcohol has been undertaken by Bolla (63, 64), who observed approximately fifty-six frequencies in ethyl alcohol. He was able to account for forty-two of these as combination frequencies with an accuracy of less than 5 wave numbers. This leaves fourteen fundamental frequencies which are as given in table 5. Of these, $\Delta\bar{\nu}$ 3632, 3359, 3240, 1618, 814, and 256 are somewhat analogous to the Raman spectrum of water. Titéica (597) considers $\Delta\bar{\nu}$ 426, 883, and 1046 as the fundamentals for the C—C oscillations, and $\Delta\bar{\nu}$ 1456, 2823, 2928, and 2974 as the fundamental C—H oscillations, $\Delta\bar{\nu}$ 1273, 2637, and 2876 being combinations. It is felt, however, that the assignments of Bolla (63, 64) are probably more compatible with the observations.

TABLE 5

Fundamental frequencies for ethyl alcohol

FREQUENCY	$\Delta\bar{\nu}$	INTENSITIES (BASIS 100)	FREQUENCY	$\Delta\bar{\nu}$	INTENSITIES (BASIS 100)
1	257	2	8	1455	46
2	433	6	9	1618	4
3	814	3	10	2879	59
4	883	60	11	2929	100
5	1051	32	12	2972	61
6	1096	27	13	3240	3
7	1274	17	14	3359	10

The polybasic alcohols have not been so widely investigated, with the exception of glycerol. Glycol, taking the average values of the observations of Whiting and Martin (645), Howlett (321), Morris (456), and Hibben (309), yields $\Delta\bar{\nu}$ 510, 660, 865 (7), 960, 1035 (5), 1070, 1090, 1260, 1465 (5), 2873 (7), 3400, where $\Delta\bar{\nu}$ 865, and possibly the 1035 to 1090 lines, are connected with the R—OH oscillation and the remainder have the significance already indicated. The $\Delta\bar{\nu}$ 3400 corresponding to the H↔O vibration is much sharper than in water or methyl alcohol, owing apparently to a more specific quantization of the vibrational energy.

Propylene glycol (456) yields $\Delta\bar{\nu}$ 830 (7), 919, 1050, 2918 (7). Glycerol has been investigated by several observers (645, 616, 516, 309, 552) and the values $\Delta\bar{\nu}$ 485, 690, 845 (7), 925, 1080, 1455 (7), and 2910 (6) obtained. There is a strong continuous scattering from glycerol attributed by Venkateswaran to its viscosity, but by Bär (26) to fluorescence on the basis of its depolarization, and by others to impurities (559). The continuous spectra decreased with increased dilution and temperature. A similar behavior in phosphoric acid solutions was noted by Hibben (309). It is certain that either fluorescent impurities or a slightly fluorescent material will be the source of a somewhat continuous spectrum. In some cases, however, the effect of temperature and dilution is so marked as to make this less probable as a universal explanation. Hibben (310) has observed that the fluorescence arising from concentrated alcoholic zinc chloride solutions can be quenched by the addition of traces of potassium iodide or nitrobenzene, which is indicative of deactivation by collisions of the second kind (Perrin).

Sugars, which may be considered in part as polybasic alcohols, have been little investigated. In view of the intense interest in the constitution of sugars from an organic or biochemical point of view, this seems rather remarkable. Kutzner (386) observed a shift at $\Delta\bar{\nu}$ 1140 in glucose and 1179 in fructose, the remaining sugars having the shift at approximately 1150. Other lines were lost behind a strong continuous spectrum. Whiting and Martin (645) obtained $\Delta\bar{\nu}$ 1090, 1480, 2870, and 3420 as the stronger lines from sucrose. Polara (516) investigated dilute solutions of a sugar, presumably glucose, and obtained the following shifts: $\Delta\nu$ 625, *668*, *689*, *858*, *945*, *1037*, 1134, 1224, 1339, *1425*, 1488, 1683, 2016, 2025, 2113, 2164, 2404, 2718, *2873*, where the italicized digits are shifts not far removed from those observed in glycol, glycerol, and propylene glycol. While low-frequency hydrogen shifts between $\Delta\bar{\nu}$ 2000 and 2600 have been observed rarely, this never has occurred at exposures which failed to bring out also the chain deformation oscillations ($<\Delta\bar{\nu}$ 650) in a molecule of this size. It seems probable, therefore, that these are either spurious or wrong assignments. The significance of $\Delta\bar{\nu}$ 1683 will be discussed later.

The investigation of characteristic frequency shifts for the alcohols is far from clear. This is primarily due to the equivalence of the hydroxyl and methyl groups. Neither the higher frequencies corresponding to the hydrogen oscillations, nor the lower frequencies corresponding to the C—OH oscillations are precisely equivalent to those observed in the hydrocarbons. Most of the intermediate frequencies, however, appear in both types of compounds. It is possible that shifts near $\Delta\bar{\nu}$ 1050 and 1300 may be connected with a carbon to oxygen vibration. Unless, however, compounds are investigated under identical conditions and with sufficient dispersion, a precise assignment of frequencies in this region is precarious. By ignoring contemporaneous data obtainable from other types of compounds one can justify the specific assignment of these shifts with some accuracy. By taking everything into consideration it is certainly possible to identify some of the alcohols in a mixture—particularly the isomeric alcohols—when it is not possible to identify the alcohols in the presence of some hydrocarbons. A further study of the O↔H vibrations in the alcohols would be of value.

D. The Raman spectra of saturated aliphatic ethers

The ethers present many of the same problems as the alcohols. An ether is an alcohol which has had its alcoholic hydrogen replaced by an organic radical. The ethers have been investigated by Lespieau (409, 410), Dadieu and Kohlrausch (173), Gopala Pai (266), Sirkar (569), Ganesan and Venkateswaran (242), Bär (25), Daure (193, 194), High (316), and others. For the most part attention has been directed primarily to diethyl ether, the observed shifts for which are $\Delta\bar{\nu}$ 375 (0), 440 (5), 500 (0), 840 (3), 928 (2), 1025 (1), 1077 (0), 1150 (2), 1270 (1), 1453 (5), 2693 (1), 2804 (2), 2870 (8), 2930 (6), 2978 (4). For dimethyl ether the values $\Delta\bar{\nu}$ 333 (0), 416 (0), 930 (2), 1102 (0), 1160 (1), 1455 (1), 2814 (7), 2869 (3), 2920 (3), 2955 (2), 2990 (4) were observed. Dipropyl, diisopropyl, diamyl, and diisoamyl ethers have been investigated by High (316). The hydrogen spectrum of these ethers consists primarily of three lines located near $\Delta\bar{\nu}$ 2865, 2920, and 2960, the lower frequency shifts beginning with $\Delta\bar{\nu}$ 930 in dimethyl ether become $\Delta\bar{\nu}$ 840 in diethyl, 790 in isopropyl, and 765 in amyl and isoamyl ethers in the same fashion as has been observed previously for the outer vibration of a unit on the end of a chain. Either dipropyl ether is an exception or else the expected shift at approximately $\Delta\bar{\nu}$ 820 was not recorded. With the exception of dimethyl ether and the iso ethers all the remainder have shifts at approximately $\Delta\bar{\nu}$ 1280. There are no shifts recorded between 1150 and 1450 for diisopropyl or diisoamyl ethers. This makes it quite easy to distinguish the presence of the iso forms. There is a fairly strong similarity between the spectra of the alcohols and the equivalent ethers, although the intensities of the lines obtained from the ethers in the region below $\Delta\bar{\nu}$ 1450 are relatively much weaker than for the equivalent lines in the alcohols. Gopala Pai (266) has attempted to calculate the valence angle of the oxygen in dimethyl ether on the assumption that it is a symmetrical triatomic molecule. Its valence angle is calculated to be 102° (which is near the tetrahedral angle of 109.5°), from the observed fundamental Raman frequencies of $\Delta\bar{\nu}$ 1102, 921, and 416. On the other hand, similar calculations for ethylene oxide, assuming $\Delta\bar{\nu}$ 1115, 865, and 810 as the fundamentals, yield a value of only 61° as the angle calculated. This large decrease in the oxygen valence angle is because of the bond between the two carbons in ethylene oxide. This view is supported by the relatively permanent dipole moments of these compounds.

Titéica (597) considers the fundamental frequencies for diethyl ether (corresponding to $\nu_1 \nu_2 \ldots$) as $\Delta\bar{\nu}$ 927, 1148, 494, 540, 438, 840, 375 for the C—C and $\Delta\bar{\nu}$ 1455, 2930, 2866, 2978 as the fundamentals for the C—H. The combination frequencies are $\Delta\bar{\nu}$ 1038, representing $\nu_3 + \nu_4$, and $\Delta\bar{\nu}$ 1077, a higher harmonic of ν_4, and finally $\Delta\bar{\nu}$ 1270, a combination of ν_5 and ν_6.

A series of the ethylene oxides has been investigated by Lespieau and Grédy (409). The ethylene oxides will be considered here even though they are cyclic compounds which have been reserved for later treatment. It is believed that they more properly may be considered ethers. Frequencies observed for ethylene oxide are $\Delta\bar{\nu}$ 808 (8), 869 (8), 1119 (5), 1269 (7), 2917 (7), 2959 (7), and 3009 (7). On comparing this with dimethyl ether it is observed that the spectra are remarkably different. There are only three lines which even approximately have any similarity. These are $\Delta\bar{\nu}$ 869—which is $\Delta\bar{\nu}$ 830 in dimethyl ether—and the two hydrogen vibrations, $\Delta\bar{\nu}$ 2917 and 2959, which are approximately the same in dimethyl ether. It is particularly noteworthy that $\Delta\bar{\nu}$ 1450, observed in all the alcohols, ethers, and hydrocarbons, with the exception of methane, is entirely absent. One would expect on substituting ethylene oxide with a side chain that the resulting spectra would have some shifts in common with the hydrocarbon radical and the increased mass would have a tendency to decrease the outer vibrations. This apparently is the case. For ethylethylene oxide the following shifts are obtained: $\Delta\bar{\nu}$ 405 (2), 455 (1), 475 (1), 732 (5), 762 (2), 802 (2), 835 (8), 905 (8), 957 (1), 1021 (1), 1051 (1), 1110 (2), 1264 (9), 1415 (2), 1456 (6), 1487 (2), 2887 (2), 2925 (10), 2945 (10), 2976 (5), 3002 (5), 3055 (2). The comparison spectra of the ethylene oxides investigated are given in figure 8.

It can be seen from the numerical values given, that the effect of the introduction of the ethyl group is to produce a number of frequencies in the region between $\Delta\bar{\nu}$ 900 and 1100, $\Delta\bar{\nu}$ 1456 and 1487 as a doublet, and $\Delta\bar{\nu}$ 2887 as well as some additional lower frequencies. The $\Delta\bar{\nu}$ 1456, as has been pointed out previously, owes its origin to the transverse motion of the hydrogen. The frequency of this transverse motion is considerably reduced when the hydrogen is attached to a ring carbon, but immediately reappears in its usual position following the substitution of a side chain containing a hydrogen attached to a carbon outside the ring structure. The $\Delta\bar{\nu}$ 2887 would seem to owe its presence to the linear oscillation of a hydrogen atom attached to a chain CH_2 group, since it is absent in 1,2-dimethylethylene oxide. On the other hand, it is present in 1,1-dimethyl-

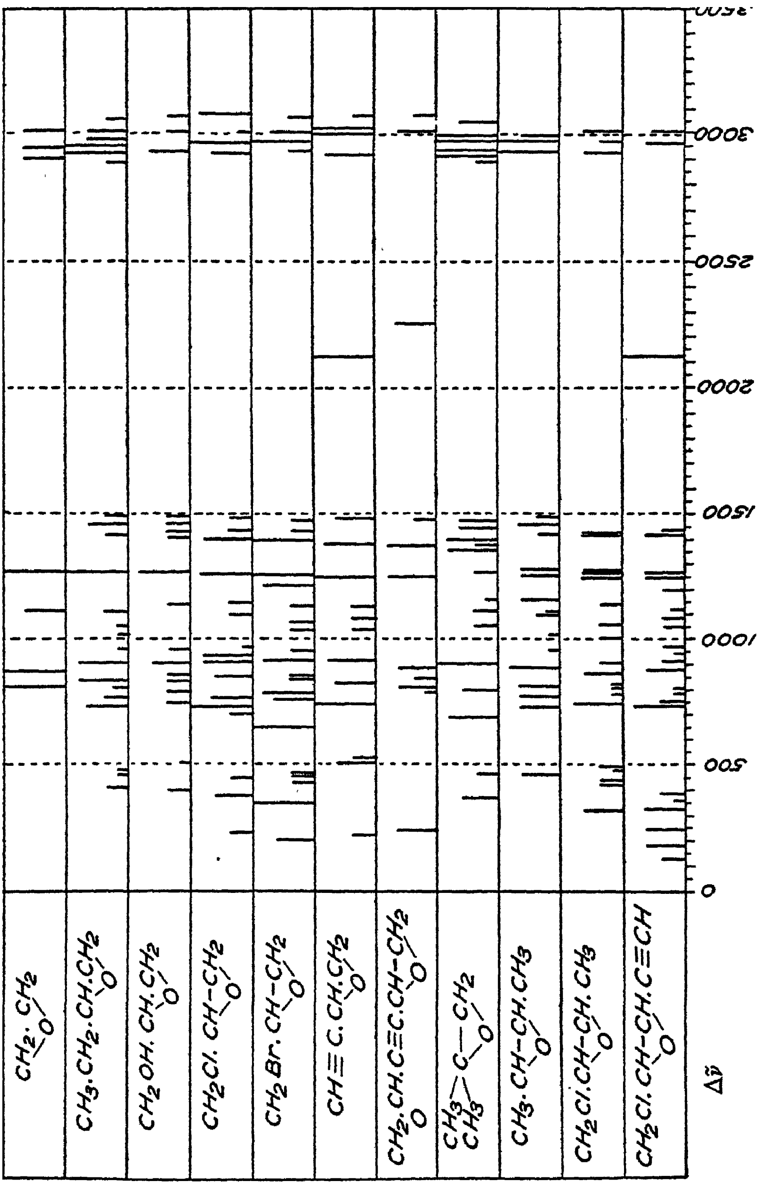
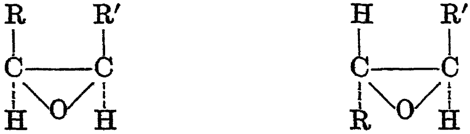


FIG. 8. Comparison spectra of ethylene oxides (after Lespieau and Grédy)

ethylene oxide. The most consistent shift is the one at $\Delta\bar{\nu}$ 1265, which remains unchanged practically throughout the series except for a doubling effect, and must be considered, therefore, the most characteristic vibration of this inner ring structure. It is strong and easily identified. The other outstanding characteristic is the first appearance of the hydrogen lines above $\Delta\bar{\nu}$ 3000, as will be discussed later. This is a characteristic of hydrogens attached to a ring or to an ethylenic linkage and is consequently present in cyclopropane and benzene. Apparently the introduction of an acetylene radical in a side chain produces a number of very low frequency oscillations all out of proportion to the masses involved. The number of frequency shifts in the region below $\Delta\bar{\nu}$ 600 is fewer when the molecule is symmetrically balanced. For the disubstituted ethylene oxides the $\Delta\bar{\nu}$ 1269 becomes double (1256–1277). Lespieau and Grédy attribute this doubling to the presence of two stereoisomers which give a spectrum consisting of two distinct lines. These isomeric forms are:



The spectra of the ethers are very close in general to the spectra obtained from the alcohols and the hydrocarbons. The addition of an oxygen is in some respects quite similar to the addition of a carbon. Nevertheless, there are considerable differences in particular lines between the ethers and the other compounds so far described. The iso ethers, like the iso alcohols, have marked differences in their spectra from the spectra of the normal compounds. The cyclic ethers have spectra more nearly like those of the cyclic hydrocarbons.

So far the Raman spectra of alcohols, ethers, and hydrocarbons have been considered as a function of constitution. It has been shown that they vary not only in a particular homologous series but also among themselves. From the evidence so far presented it is possible to calculate the force exerted between the atomic constituents of the molecules under normal conditions and in simple cases their relative configuration. Furthermore, the type of vibrations which give rise to certain frequencies is quite clear. The effect of substitution on these frequencies is notable and can be calculated if the molecules are not too complex. If the substituent group is markedly different in mass, or if the force constant between the carbon and a substituent atom or group is markedly different, it has a pronounced effect on Raman spectra obtainable from the molecules. This is clear in the case of the halogen substitutions. When the

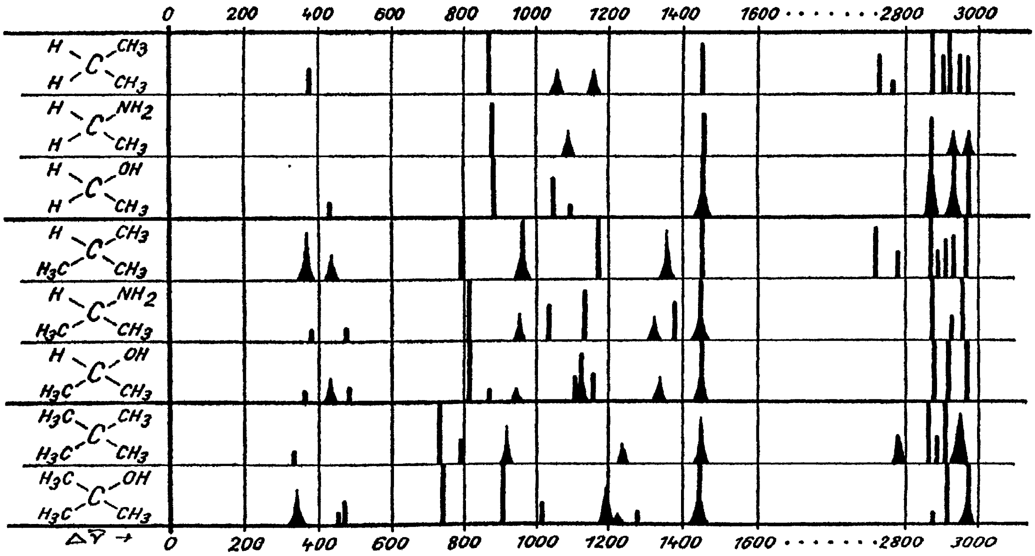


Fig. 9. The effect of substitution on some simpler hydrocarbons (after Kohlrausch, Pongratz, and Seka)

mass and the force constants remain very much the same it is more difficult, but not impossible, to distinguish the effect of the substitution in a not too complicated mixture. In figure 9 are shown the effects of different substituent groups on similarly constituted hydrocarbons, as taken from the summary of Kohlrausch, Pongratz, and Seka (369).

It is to be emphasized most strongly that the discussion thus far rests primarily upon the magnitude of the Raman shift. There are two other parameters, however, which may be invoked to describe the type or character of oscillations besides the actual displacements. These are the intensities, which have been given only roughly, and the degree of depolarization. As has been pointed out, in Raman spectra the symmetrical oscillations are the most intense and most strongly polarized; this is reflected in the smallest depolarization constant. In comparing, for example, the types of oscillations which will give rise to Raman lines in bromoform or chloroform, even though the magnitude of displacement may be radically different, it is possible to distinguish from their degree of depolarization what lines are attributable to a symmetrical oscillation.

As the hydrocarbon radical will present a more or less constant rôle, for future considerations the remainder of the treatment of Raman spectra from hydrocarbons and their derivatives will be based mainly on the effects of types of linkage rather than on complete spectra. This is for a twofold purpose: first, because the effects of substitution on the linkage are made more clear if the summary is confined to the linkage involved, and second, because of space and time considerations. Recourse may be had to the indices for complete details on every compound. In most cases it is sufficient to illustrate the correlation between Raman spectra and the types of linkage without discussing in complete detail the entire Raman shifts for every compound studied.

E. Raman spectra and the ethylenic linkage

It has already been shown that a pronounced effect upon a single bond takes place on the substitution of atoms of a quite different nature from the organic radicals. In the case of the ethylenic linkage this effect is equally pronounced and much more easily measurable. The Raman spectrum for $C{=}C$ falls in the region of $\Delta\bar{\nu}$ 1600 to 1650 more or less completely separated from any lines due to any other type of oscillation. The lines are sharp and can be measured with accuracy. Therefore, the effects of mass and of the binding force of the atoms in the molecule can be determined with considerable exactness. The reason for this unique displacement is that the force constant is roughly twice that involved in a single bond and hence carries the emission to a region free from other Raman lines. This opens up a more or less endless avenue in the investigation of constitutional problems where ethylenic linkages are involved. An example of this is in the terpenes, which will be discussed later, and in the identification of various isomers. It may be stated categorically that any straight chain compound and most cyclic compounds having the structure $-\overset{|}{C}=\overset{|}{C}-$ will show a Raman shift in the 1600 region. If the structure is $-\overset{|}{C}=C=\overset{|}{C}-$, however, this is not true and the characteristic shift will fall elsewhere, for reasons which will be explained later. Most of this evidence is empirical, although in the simpler ethylenic hydrocarbons one can calculate quite easily the relative forces and spacial configurations. The empirical approach nevertheless is the same approach by which the chemist knows that barium sulfate is precipitated on the addition of barium salts to a solution containing soluble sulfates. The physicist might rest more tranquilly if the cloak of respectability could be given these procedures by clothing them with eigenfunctions and Greek letters. Nevertheless the probabilities are, under these conditions, that barium sulfate is the precipitate. Likewise the appearance of a Raman shift in the region between $\Delta\bar{\nu}$ 1600 and 1650 is equally indicative of a double linkage in this type of compound.

In table 6 are given the Raman shifts of many of the ethylenic hydrocarbons. In some cases the studies have not been complete, and in other cases the relative intensities have not been recorded. In table 7 are given the Raman shifts for some of the ethylenic hydrocarbons as a function of substitution. It has been observed that substitution affects the saturated hydrocarbons, particularly in the lower frequencies and occasionally in the higher frequencies. This is easily discernible with the ethylenic hydrocarbons by the reaction on the double-bond linkage. The ethylenic hydrocarbons have five shifts more or less characteristic. Those shifts in the $\Delta\bar{\nu}$ 1600 to 1650 region are correctly attributable to the C=C linkage and those between $\Delta\bar{\nu}$ 3000 and 3100 to the C—H. In the saturated hydrocarbons any frequency beyond $\Delta\bar{\nu}$ 3000 is exceptional, save those attributable to cyclic compounds. The intensity relations make it very easy to distinguish between a hydrogen attached to a double bond and the shift arising from a hydrogen in a ring structure without a double bond. Bourguel (97, 99) has indicated the effect of substitution. If one replaces the hydrogen in ethylene with a hydrocarbon radical or substituted radical the ethylenic shift $\Delta\bar{\nu}$ 1620 is increased. For example, in propylene it becomes $\Delta\bar{\nu}$ 1647. This decreases gradually, so that with benzylethylene it has become $\Delta\bar{\nu}$ 1640. If, however, a hydrogen atom in ethylene is replaced by an aldehyde group or a halogen atom the frequency is markedly reduced, becoming $\Delta\bar{\nu}$ 1608 in monochloroethylene and

TABLE 6

Raman shifts for some ethylenic hydrocarbons

COMPOUNDS	$\Delta\bar{\nu}$ 0 to 700	$\Delta\bar{\nu}$ 700 to 1000	$\Delta\bar{\nu}$ 1000 to 1500	$\Delta\bar{\nu}$ 1500 to 1700	$\Delta\bar{\nu}$ 1700 to 3000	$\Delta\bar{\nu}$ 3000 to 3200
Ethylene			1340 (3)	1620 (3)		3000 (5) 3082 (3)
Propylene (incomplete)			1295 (8) 1414 (6)	1647 (8)		3007 (7) 3086 (7)
Trimethylethylene	253 (1)* 388 (5) 444 (5) 528 (5)	767 (7) 803 (2)	1338 (7) 1383 (7) 1446 (7)	1653 (1) 1679 (8)	2732 (1) 2861 (8) 2885 (2) 2922 (10) 2973 (8)	3055 (2)
1-Pentene	386 (5) 427 (2) 628 (1)	851 (5) 881 (5) 913 (5) 993 (1)	1047 (2) 1095 (2) 1232 (2) 1296 (8) 1416 (8) 1447 (7)	1642 (8)	2847 (3) 2866 (3) 2877 (8) 2910 (8) 2938 (8) 2966 (5)	3000 (8) 3080 (8)
2-Pentene	211 (3) 412 (5) 488 (7) 578 (3) 698 (2)	752 (3) 800 (5) 860 (5) 880 (2) 943 (3) 966 (2)	1027 (5) 1066 (5) 1248 (7) 1268 (7) 1290 (7) 1310 (7) 1379 (7) 1450 (8)	1658 (7) 1674 (8)	2857 (7) 2887 (8) 2920 (10) 2941 (10) 2966 (8)	
1-Hexene	358 (2)	818 (2) 873 (1) 912 (2)	1056 (2) 1296 (7) 1417 (8) 1448 (7)	1642 (8)	2859 (5) 2876 (8) 2909 (8) 2963 (5)	3002 (8) 3076 (5)
2-Hexene (mixture)	389 (2)	857 (2) 892 (2)	1042 (2) 1095 (5) 1216 (1) 1258 (5) 1290 (5) 1308 (7) 1378 (5) 1445 (7)	1658 (5) 1674 (7)	2875 (8) 2920 (8) 2939 (7)	
4-Methyl-2-pentene	333 (2) 345 (2) 484 (5)	820 (5) 905 (2) 956 (2)	1043 (2) 1103 (5) 1256 (2) 1300 (7) 1380 (5) 1456 (7)	1659 (5) 1673 (7)	2870 (8)	

* The values for the intensities are those given in parentheses.

TABLE 6—*Continued*

COMPOUNDS	$\Delta\bar{\nu}$ 0 to 700	$\Delta\bar{\nu}$ 700 to 1000	$\Delta\bar{\nu}$ 1000 to 1500	$\Delta\bar{\nu}$ 1500 to 1700	$\Delta\bar{\nu}$ 1700 to 3000	$\Delta\bar{\nu}$ 3000 to 3200
3-Methyl-2-pentene (mixture)	320(2) 395(2) 490(5) 551(1)	749(7) 825(1) 125(1)	1071(5) 1117(2) 1255(5) 1317(2) 1350(5) 1383(7) 1451(7)	1673(8)	2852(8) 2879(8) 2920(8) 2966(7)	
2-Methyl-2-pentene	356(5) 473(2) 513(5)	745(5) 816(7) 833(7) 908(7)	1007(5) 1063(7) 1120(2) 1262(5) 1306(7) 1351(5) 1381(7) 1452(7)	1676(8)	2879(8) 2912(8) 2932(8) 2964(7)	
2,5-Dimethyl-2-hexene (incomplete)		702 769 805 848 949	1107 1264 1328 1376 1445	1669		
3,5-Dimethyl-3-hexene (incomplete)		775 844 956	1032 1120 1282 1327 1380 1450	1667		
3,6-Dimethyl-2-heptene (incomplete)		803 840 953	1025 1108 1330 1381 1449	1668		
4,6-Dimethyl-3-heptene (incomplete)		804 954	1038 1103 1295 1327 1380 1452	1667		
2,3,5-Trimethyl-2-hexene (incomplete)		850 958	1105 1330 1382 1454	1667		

TABLE 6—*Concluded*

COMPOUNDS	$\Delta\bar{\nu}$ 0 to 700	$\Delta\bar{\nu}$ 700 to 1000	$\Delta\bar{\nu}$ 1000 to 1500	$\Delta\bar{\nu}$ 1500 to 1700	$\Delta\bar{\nu}$ 1700 to 3000	$\Delta\bar{\nu}$ 3000 to 3200
2,4-Dimethyl-2-octene (incomplete)		786 862 955	1103 1163 1295 1328 1377 1450 1465			
2-Methyl-2-octene	187(5) 403(7) 445(3)	761(2) 795(2) 852(3) 893(5) 968(3)	1017(1) 1110(5) 1302(7) 1320(5) 1383(10) 1442(10)	1677(8)	2800(10) 2975(10)	
3-Methyl-2-octene (incomplete)	166(1)		1072(5) 1117(5) 1170(5) 1258(1) 1299(5) 1360(1) 1380(5) 1445(10)	1671(9)	2855(10) 2876(5) 2899(5) 2920(7) 2940(7) 2966(10)	
2,4,6-Trimethyl-3-heptene (incomplete)		702 797 860 956	1102 1165 1300 1329 1377 1449	1665		
2,4,7-Trimethyl-4-octene (incomplete)		952	1098 1283 1329 1375 1448	1663		

$\Delta\bar{\nu}$ 1595 in monobromoethylene. If the effects of different substituents be compared, it is evident that a hydrocarbon substituent on the one hand and an alcohol or a halogen on the other reacts on the C═C linkage in the opposite sense. Furthermore, if the substitution takes place in the β-position in reference to the double bond, the effect is much less marked than in the α-position. This is in accord with the classical organic theory, in regard to the continuing effect of substitution in the hydrocarbon chain.

1. Cis-trans isomerism

The compounds given in table 7 are essentially those of the type R—$CH=CH_2$. The question now is what effect on the C═C shift have substitutions of the type R—CH═CH—R′. This brings immediately to the fore the problem of *cis-trans* isomerism. The isomers of this type examined earliest were the 1,2-dichloroethylenes, studied by Bonino and Brüll (77), and the geometrical isomers ethyl fumarate and ethyl maleate which were investigated by Ffolliott (231). Pestemer (496), and Dadieu, Pongratz, and Kohlrausch (180, 181, 182, 183) have also considered the *cis-trans* isomerism in halogen and oxygen derivatives of ethylene. Apparently the effect on the ethylenic linkage is rather small in these types of compounds. There is, however, a pronounced change in the spectra, particularly in reference to the middle and lower frequency shifts. In table 8 are given recent results of Trumpy (608) with dichloroethylene. It is observable that there is considerable difference between the spectra of the two compounds.

TABLE 7

Raman shifts characteristic of C═C *and other shifts common to olefins*

SUBSTANCE	$\Delta\bar{\nu}$						
$CH_2=CH\cdot H$		1340			1620	3000	3080
$CH_2=CH\cdot CH_3$	1295		1414		1647	3007	3086
$CH_2=CH\cdot C_2H_5$	1294		1416		1642	3003	3083
$CH_2=CH\cdot C_3H_7$	1296		1416		1642	3001	3079
$CH_2=CH\cdot C_4H_9$	1295		1416		1642	3002	3076
$CH_2=CH\cdot C_5H_{11}$	1299		1416		1642	3000	3081
$CH_2=CH\cdot C_6H_{13}$	1296		1416		1642	3001	3081
$CH_2=CH\cdot CH_2\cdot C_6H_5$	1296		1413		1642	3006	3067
$CH_2=CH\cdot C_7H_{15}$	1300		1416		1642	3003	3081
$CH_2=CH\cdot CH_2\cdot C\equiv C\cdot C_6H_5$			1416		1642		
$CH_2=CH\cdot CH_2OH$	1290		1416		1646	3014	3089
$CH_2=CH\cdot CHOH\cdot CH_3$	1287		1416		1646	3013	3089
$CH_2=CH\cdot CHO$	1277		1363		1618		
$CH_2=CH\cdot COOH$	1288		1397		1638		3111
$CH_2=CH\cdot Cl$	1271		1355		1608	3036	3134
$CH_2=CH\cdot CH_2Cl$	1291		1411		1640	3022	3090
$CH_2=CH\cdot CH_2Br$	1295		1409		1635	3016	3089
$H_2C=CH\cdot CH=CH_2$	1277		1436		1634	3000	3090
$H_3C\cdot CH=CH\cdot CH=CH_2$	1288		1443	1597	1646	2998	3089
$H_2C=C(CH_3)\cdot CH=CH_2$	1291		1420		1640	3012	3090
$H_2C=CHCH_2CH=CH_2$	1295		1413		1644	3010	3084
$H_2C=CHCH_2CH_2CH=CH_2$	1298		1416		1641	3004	3081

In the hydrocarbons, however, on account of the multiplicity of lines in the lower frequency regions, it is much more important to ascertain if there is an effect on the C=C linkage which can be clearly observed. Bourguel, Grédy, and Piaux (104) examined some of the substituted unsaturated hydrocarbons, with the results presented in table 9. The *cis*-ethylenic compounds of the type R—CH=CH—R′, where R′ is an ethyl group, give $\Delta\bar{\nu}$ 1658. In the corresponding *trans*-forms, however, the shift becomes $\Delta\bar{\nu}$ 1674. If R′ is a phenyl group in lieu of an ethyl group the external C=C shift is decreased and becomes $\Delta\bar{\nu}$ 1642 for the *cis*-form and $\Delta\bar{\nu}$ 1664 for the *trans*. In all cases the *trans*-compound has a shift greater by 15 wave numbers than the *cis*-compound. The band between $\Delta\bar{\nu}$ 1255 and 1260 in the *cis*-compound is slightly elevated and $\Delta\bar{\nu}$ 1376 appreciably stronger in the *trans*-compound. This work has been repeated by Grédy (281) with similar results. Grédy and Piaux (283) have examined the *cis*- and *trans*-forms of crotonyl acetate, methylvinylcarbinol acetate, crotonyl alcohol, methylvinylcarbinol, crotonaldehyde, 1-methylallyl bromide, and 2-butenyl bromide. For the aldehyde $\Delta\bar{\nu}$ 1647 is attributed to the *trans*-form and $\Delta\bar{\nu}$ 1625 to the presence of 1 per cent of the *cis*-form. Similarly with the crotonyl alcohol, $\Delta\bar{\nu}$ 1677 and a very feeble $\Delta\bar{\nu}$ 1657 shift are attributed to the *trans*- and *cis*-forms. Methylvinylcarbinol yields $\Delta\bar{\nu}$ 1647, and crotonyl acetate $\Delta\bar{\nu}$ 1664 *cis* and $\Delta\bar{\nu}$ 1679 *trans*, and methylvinylcarbinol acetate $\Delta\bar{\nu}$ 1648. The bromine derivative, 1-methylallyl bromide, yields $\Delta\bar{\nu}$ 1638; 2-butenyl bromide yields $\Delta\bar{\nu}$ 1651 *cis*, and $\Delta\bar{\nu}$ 1665 *trans*. This is in contrast to $\Delta\bar{\nu}$ 1646 observed for allyl alcohol, and $\Delta\bar{\nu}$ 1635 for allyl bromide. Bourguel (97) notes that the

TABLE 8

The Raman effect in two isomeric derivaties of ethylene

cis-DICHLOROETHYLENE			*trans*-DICHLOROETHYLENE		
$\Delta\bar{\nu}$ cm.$^{-1}$	i	ρ	$\Delta\bar{\nu}$ cm.$^{-1}$	i	ρ
171	18	0.50	350	20	0.29
407	10	0.82	752	5	0.7
561	5	0.88	840	6	0.08
711	15	0.05	1271	15	0.2
806	0.5		1575	10	0.07
880	1	D	1625	0.5	P
1180	10	0.7	1690	1	P
1586	15	0.08	3072	10	0.2
1688	2		3140	1	
3078	20	0.31			
3158	1				

ethylenic linkage shift is increased by disubstitution, but this augmentation is less if the two substituent groups are on the same carbon than if they are on different atoms. For the external double bond in limonene is observed Δν̄ 1647, in 2-methyl-1-butene Δν̄ 1652, in 2-pentene Δν̄ 1657, and in cyclohexene Δν̄ 1654. In trisubstituted products such as trimethylethylene, Δν̄ 1679 results, and in the intranuclear double bond in limonene it is likewise Δν̄ 1679. Comparison of the effect of halogen substitution

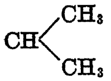
TABLE 9

Some Raman shifts in cis-trans isomers of unsaturated hydrocarbons

COMPOUNDS	Δν̄		
cis-2-Pentene	1248–1266 (7)	1375 (2)	1658 (10)
trans-2-Pentene	1298–1313 (7)	1378 (7)	1674 (10)
cis-2-Octene	1256 (7)	1376 (2)	1658 (10)
trans-2-Octene	1305 (7)	1379 (7)	1673 (10)
cis-2-Nonene			1658 (10)
cis-2-Cyclohexyl-6-hexene	1260 (7)		1657 (10)
cis-1-Phenyl-1-propene	1192 (7)	1373 (2)	1642 (10)
trans-1-Phenyl-1-propene	1210 (7)	1378 (7)	1664 (10)

TABLE 10

The effect of disubstitution on the C═C *shifts*

RADICAL R	CH_2═CH—R	CH_3—CH═CH—R		RADICAL R	CH_2═CH—R	CH_3—CH═CH—R		
		cis	*trans*			*cis*	*trans*	
CH_3	1647			$CH_2C≡CC_6H_5$	1642			
$CH_2O(COCH_3)$	1649	1665	1679	$CHClCH_3$	1640			
CH_2OH	1646	1658	1677	$CH_2C_6H_5$	1640			
$CHOHCH_3$	1646			CH_2Cl	1640		1671	
CHOHC≡CH	1646		1676	$CHCl_2$			1666	(Kirrmann)
$CHOHCH{=}CH_2$	1646		1674	$CHBrCH_3$	1635	1651	1666	
C_2H_5	1642	1658	1674	COOH	1638	1645	1652	(Kohlrausch)
C_3H_7	1642	1658	1674	COOR		1644	1655	
C_4H_9	1642	1658	1674	C_6H_5	1631	1642	1665	
C_5H_{11}	1642	1658	1674	H	1620	1647		
C_6H_{13}	1642	1658	1674	CN		1628	1645	(Kohlrausch)
C_7H_{15}	1642			CHO	1618	1625	1642	
				Cl	1608			
 $CH(CH_3)_2$		1659	1673	Br	1598			
$CH_2C_5H_9$	1642	1658	1674					
$(CH_2)_3C_6H_{11}$		1657						

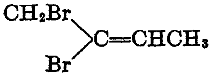
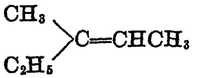
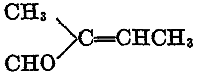
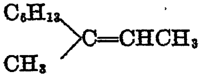
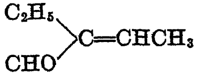
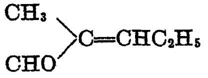
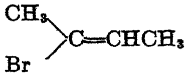
in 2-bromohexene with 1-hexene shows that this results in a retardation of the frequency from $\Delta\bar{\nu}$ 1642 to 1632.

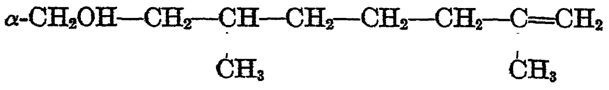
Grédy (281) has summarized some of these conclusions on the effect of disubstitution as given in table 10. Risseghem, Grédy, and Piaux (544), and Grédy (282) obtained the results with trisubstituted ethylenes as given in table 11.

The precise shifts attributed to ethylenic double bonds have been considered in some detail, because of their utility in determining the structure of the terpenes, styrenes, furans, and similar compounds. It is quite possible to determine the composition of mixtures containing *cis*- and *trans*-isomers and to follow their transitions from one form to the other. It is likewise possible to follow the change in composition on the distillation of various olefins and terpenes, all of which has not only a bearing upon the constitution of the molecule involved but also a practical importance in relation to the effect of chemical treatment and fractionation of these compounds. An example of the delineation of structure in a mixture is in the observations of Grédy (273) and of Naves, Brus, and Allard (470) on the isomerism of rhodinol and citronellol. The two forms known are:

TABLE 11

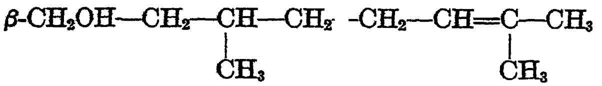
The Raman shifts in some trisubstituted ethylenes

COMPOUND	$\Delta\bar{\nu}$	COMPOUND	$\Delta\bar{\nu}$
$(CH_3)_2C{=}CHCH_3$	1679		1648
	1773		1648
	1671		1647
$(CH_3)_2C{=}CHC_2H_5$	1676		1645
$(CH_3)_2C{=}CHC_5H_{11}$	1677		
$(CH_3)_2C{=}C(CH_3)_2$	1676		
	1658		



$$\alpha\text{-}CH_2OH{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH_2{-}\underset{CH_3}{C}{=}CH_2$$

Type $R_1R_2C{=}CH_2$ ($\Delta\bar{\nu}$ 1650)



$$\beta\text{-}CH_2OH{-}CH_2{-}\underset{CH_3}{CH}{-}CH_2{-}CH_2{-}CH{=}\underset{CH_3}{C}{-}CH_3$$

Type $RCH{=}CR_1R_2$ ($\Delta\bar{\nu}$ 1678)

It was found that compounds of the type of 2-methyl-1-octene yield $\Delta\bar{\nu}$ 1647 and compounds of the type of 3-methyl-2-nonene yield $\Delta\bar{\nu}$ 1672. These are analogous to the α- and β-forms. Citronellol gives $\Delta\bar{\nu}$ 1677 with a very faint line at 1645, and from this it is probably correctly concluded that in this compound the β-form is predominant.

F. The Raman spectra of the diolefins

In table 7 were given some of the characteristic shifts of the diolefins as compared with the monoölefins. It is to be expected that the substitution of a hydrocarbon group for a hydrogen next to one of the double bonds would cause an increase in the characteristic C=C linkage. In butadiene the shift is $\Delta\bar{\nu}$ 1634 and in 1,3-pentadiene $\Delta\bar{\nu}$ 1646 as compared with ethylene ($\Delta\bar{\nu}$ 1620). In 3-methyl-1,3-butadiene the increase is less marked, the resulting shift being $\Delta\bar{\nu}$ 1640. In general the effect of conjugation on the normal ethylenic linkage is to produce a fairly constant frequency shift in the region of $\Delta\bar{\nu}$ 1644. Bourguel (100) and Piaux (508) postulate that the effect of conjugation is to reduce the ethylenic frequency over what would be expected theoretically. Multiple conjugation such as found in benzene and styrene can best be discussed under cyclic compounds, because one must consider here not only the influence of multiple conjugation but also the effect of the ring. Until the contribution of the ring has been dealt with, consideration of this aspect of the ethylenic double-bond frequency is postponed. There is, however, one other phase of conjugation which properly belongs in the discussion of olefinic derivatives of hydrocarbons. This is the interesting problem of the allenes.

The allenes have a general structure RC=C=CR′. On first inspection it would seem that the thesis so far presented regarding the relative constancy of the shift in the region of $\Delta\bar{\nu}$ 1640 for a doubly bound carbon was not tenable, as this shift is entirely absent in the allenes. Indeed, in a strict interpretation this is apparently true. There do appear, however, other shifts in the region of $\Delta\bar{\nu}$ 1080 to 1130 which are quite characteristic of these compounds. The explanation of the displacement of $\Delta\bar{\nu}$ 1640 to the $\Delta\bar{\nu}$ 1100 region as characteristic of the double-bond carbon in this type of compound is both reasonable and consistent. The ethylenic shift $\Delta\bar{\nu}$ 1640 is considered an inner vibration, that is, only depending secondarily upon the mass relationship in the rest of the molecule. In calculating the force constant from the observed frequency displacement and the reduced masses or vice versa for the C=C linkage only the relative masses of the two carbons are taken into consideration. In the case where the double bond is attached to the same carbon atom as in the allenic compounds this is no longer true. If it is assumed that the relative vibrating masses in this case are not simply two carbon atoms but three carbon atoms, then from equation 2 the ratio of the expected frequencies is

$$\frac{\Delta\bar{\nu}_1}{\Delta\bar{\nu}_2} = \frac{1}{\sqrt{2}}$$

If $\Delta\bar{\nu}_2$ is $\Delta\bar{\nu}$ 1625, then $\Delta\bar{\nu}_1$ will be $\Delta\bar{\nu}$ 1145. This is not greatly removed from the observed frequencies. When substitution in the allenes takes place there appear two frequencies, one near $\Delta\bar{\nu}$ 1130 and one in the region of $\Delta\bar{\nu}$ 1090 to 1070. It is to be admitted that in allene the shift $\Delta\bar{\nu}$ 1073 is not in entire agreement with this hypothesis, but no allowance has been made for a possible change in value of the force constant which could account for this discrepancy. The appearance of two frequencies in the unsymmetrical substituted derivatives is reasonable in view of the possible perturbations as a result of the disymmetry.

In any case the allenic compounds have a well-defined shift or shifts quite characteristic of their structures, and it is believed that this explanation of the displacement of the usual shift is not far removed from the correct one. These compounds have been investigated by Bourguel and Piaux (105, 106), by Piaux (508), and by Kopper and Pongratz (371). In figure 10 are given the Raman spectra of some of the allenes.

G. Raman spectra and the carbonyl linkage

From the point of view of Raman spectra it is more logical to proceed with the discussion of similar types of linkage and their effect on the Raman shifts than to consider the compounds in the same sequence as employed in organic chemistry. There is, however, a much greater demarcation between the triple-bond and the double-bond spectra than there is between the carbonyl and the ethylenic spectra. For this reason the carbonyl spectra are considered here, and the acetylenic and cyclic compounds are considered later.

The carbonyl linkage is found in the aldehydes, ketones, acyl halides, acids, esters, and anhydrides. The magnitude of this shift varies from approximately $\Delta\bar{\nu}$ 1645 to 1800, depending on the influence of adjacent groups. While it is possible in specific instances that the lowest frequency carbonyl shifts might be confused with the higher frequency ethylenic shifts, as a rule this causes no difficulty. Since the mass of oxygen is greater than that of carbon, the increase in the frequency displacement is caused by the somewhat greater force exerted between the carbon and oxygen atoms than exists between the carbon atoms in $C{=}C$.

1. Acids. The lowest displacement for the carbonyl oscillation is in the acids. The average shift for aliphatic acids is approximately $\Delta\bar{\nu}$ 1654.

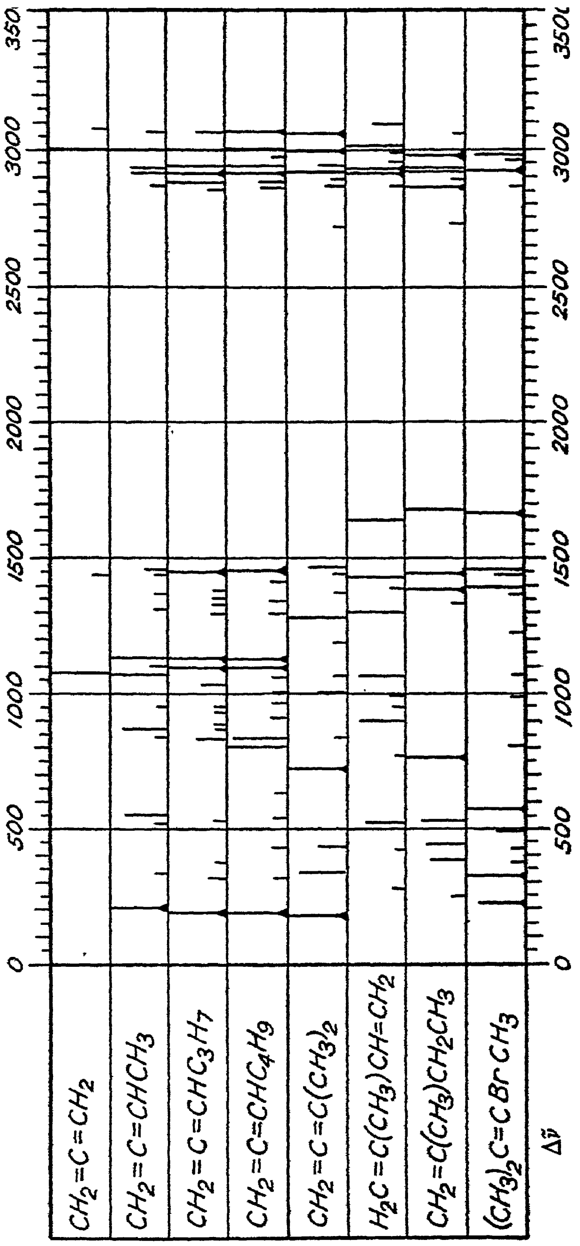


FIG. 10. The Raman spectra of some allenes and some olefins (after Lespieau and Grédy)

This frequency may be influenced, however, by side-chain substitution. A decrease in the magnitude of this shift is illustrated in the following acids: propionic $\Delta\tilde{\nu}$ 1652, butyric $\Delta\tilde{\nu}$ 1654, isobutyric $\Delta\tilde{\nu}$ 1649, trimethylacetic $\Delta\tilde{\nu}$ 1645. Formic acid is omitted, as the first member in each series of carbonyl compounds has a slightly different Raman shift for the carbonyl group in every case. The characteristic frequency shifts for the lower oscillations in the acids are given in figure 11 from the data compiled

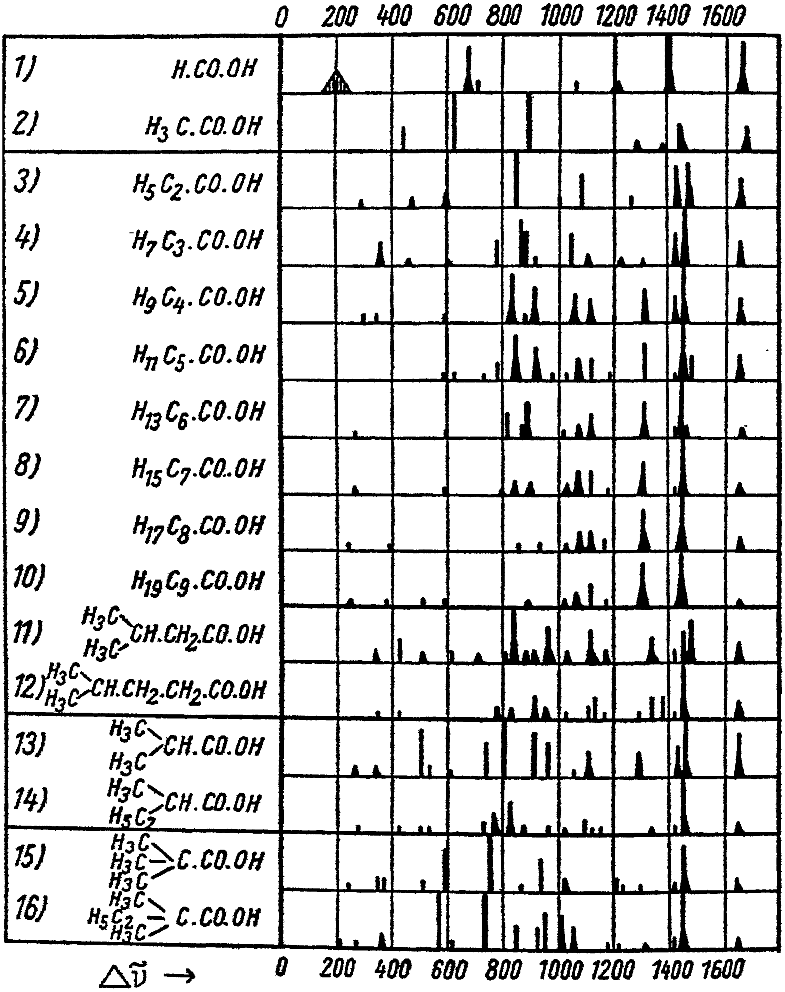


FIG. 11. The lower frequency shifts of the aliphatic acids (after Kohlrausch, Köppl and Pongratz)

by Kohlrausch, Köppl, and Pongratz (352), and Dadieu and Kohlrausch (152, 158). The shift in the region of $\Delta\bar{\nu}$ 1440 appears even in formic acid (489) at $\Delta\bar{\nu}$ 1400. This shift, corresponding to the usual bending moment of the hydrocarbon, appears as a doublet and in some cases as a triplet practically throughout the series. In the isomeric acids there appear strong frequency shifts between $\Delta\bar{\nu}$ 500 and 800. In pivalic acid there are two, $\Delta\bar{\nu}$ 589 (4) and 753 (10), and in α,α-dimethylbutyric acid $\Delta\bar{\nu}$ 575 (5) and $\Delta\bar{\nu}$ 736 (8). The very broad band appearing in formic acid at $\Delta\bar{\nu}$ 200 is unique for a molecule of this size. There are a large number of fairly strong hydrogen lines. For acetic acid the values are $\Delta\bar{\nu}$ 2937 (10), 2986 (1), and 3033 (1), but for propionic acid and the remainder of the series there appear at least four or five fairly strong hydrogen lines (352, 618). The first of these, $\Delta\bar{\nu}$ 2756 (2), is the weakest. The $\Delta\bar{\nu}$ 2756 in propionic acid is 2739 in butyric, absent in isobutyric, $\Delta\bar{\nu}$ 2730 in valeric, and 2729 in caproic acid. The $\Delta\bar{\nu}$ 2888 (4) in propionic acid becomes 2875 (9) in butyric acid and remains fairly constant at this frequency throughout the series. The shift $\Delta\bar{\nu}$ 2921 (6) in propionic acid decreases to $\Delta\bar{\nu}$ 2912 in butyric acid, and thereafter is practically unaltered. The $\Delta\bar{\nu}$ 2944 (12) in propionic acid decreases slightly until it becomes $\Delta\bar{\nu}$ 2935 in caproic and 2930 in pelargonic acid; $\Delta\bar{\nu}$ 2986 (8) decreases with increased chain length until in caprylic acid it is reduced to $\Delta\bar{\nu}$ 2963.

TABLE 12

Influence of substitution on the carbonyl frequencies

SUBSTANCE	$\Delta\bar{\nu}$				
	H_3CCOX	RH_2CCOX	R_2HCCOX	R_3CCOX	C_6H_5COX
Acid, X = OH	1666	1652	1648	1644	1647
Methyl ester, X = OCH_3	1736	1735	1732	1728	1720
Ethyl ester, X = OC_2H_5	1736	1732	1728	1724	1721
Ketone, X = CH_3	1710	1709	1709	1702	1677
Acid chloride, X = Cl	1798	1793	1788	1790	
Aldehyde, X = H	1715	1719	1719	1723	1689

The effect of substituting halogens in the molecule to form the chloroacetic acids has been studied by Cheng (124), Ghosh and Kar (248), Thatte and Ganesan (592), Woodward (664), and Parthasarathy (490). The carbonyl frequency is considerably augmented and decreased somewhat in intensity. It becomes a broad band from $\Delta\bar{\nu}$ 1675 to 1740 in the monosubstituted acid and splits into two lines corresponding to $\Delta\bar{\nu}$ 1678 and 1740 in the disubstituted acid and $\Delta\bar{\nu}$ 1682 and 1740 in the trisubstituted acid. The intensity in all cases is not relatively greater than two.

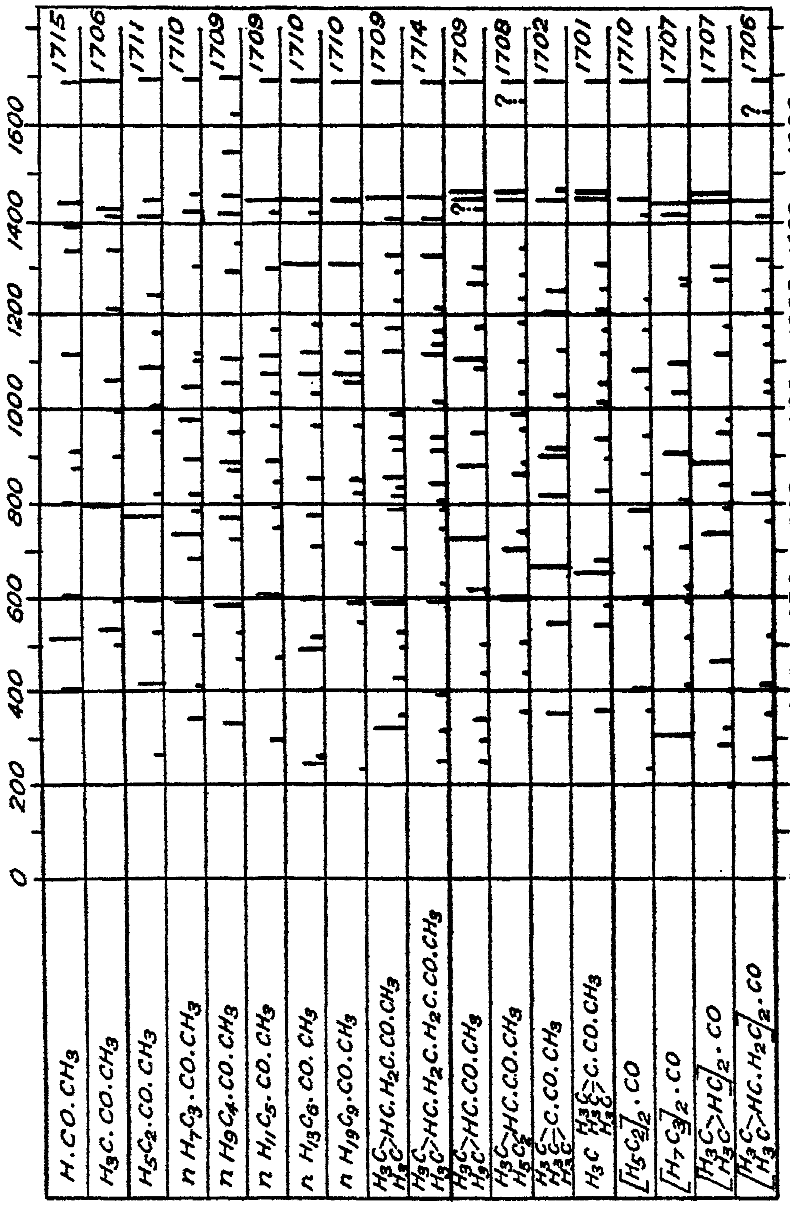


FIG. 12. The lower frequency Raman spectra of aliphatic ketones (after Kohlrausch and Köppl)

2. Ketones. The aliphatic ketones have a slightly greater displacement than the acids and slightly less than the aldehydes. On the average the frequency shift is approximately $\Delta\bar{\nu}$ 1710 for the aliphatic ketones. Substituting aliphatic radicals on the carbon atom in the α-position to the carbonyl group slightly diminishes the carbonyl frequency. In general this is true for all the carbonyl compounds and is illustrated in table 12. In compounds of the type X—CO—R the relative influences of different radicals are respectively in the following order (342, 366): C_6H_5, CH_3, C_2H_5, H, OR′, and Cl. If X represents any of these groups and Y is replaced by these groups in the order given, the frequency will increase. The converse is true, of course, if Y is held constant and X is replaced. If both are replaced the frequency will also increase if the replacement is in the order given.

The diminution of frequency influence in the ketones by the substitution of aliphatic radicals is given in figure 12. Nevertheless, the effect of isomerism is not negligible in methyl *tert*-butyl ketone. The carbonyl frequency is 8 wave numbers less than that of the corresponding straight chain aliphatic compounds. Cheng and Lecomte (127) have investigated the halogen derivatives of the ketones.

3. Aldehydes. The next in the series of the carbonyl frequencies are the aldehydes. The carbonyl frequencies corresponding to the aldehydes are in the immediate neighborhood of $\Delta\bar{\nu}$ 1720 and remain constant within a few wave numbers of this value in the entire homologous series. There is apparently a slight increase amounting to not more than 10 wave numbers brought about by the substitution of methyl groups in place of the hydrogen on the α-carbon atom. This is shown in table 12. The aldehydes have been investigated in detail by Kohlrausch and Köppl (348).

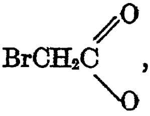
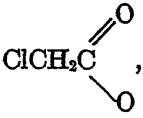
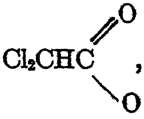
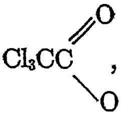
Formaldehyde in solutions containing a large excess of the formaldehyde, or in the gaseous state, apparently has a shift corresponding to $\Delta\bar{\nu}$ 1768. An interesting phenomenon was observed, however, by Hibben (309). If formaldehyde is dissolved in water so that the concentration is not in excess there is no carbonyl frequency obtainable. The spectrum has a relatively close similarity to that of glycol, pointing to the formation in solution of methylene glycol ($CH_2O + H_2O \rightleftarrows CH_2(OH)_2$). These results have been confirmed by Krishnamurti (376). In paraformaldehyde Hibben (309) has also noted that there is no carbonyl shift similar to the result obtained with paraldehyde by Venkateswaran and Bhagavantam (627). It was also supposed that the paraldehyde, and possibly in this case the paraformaldehyde, formed a ring structure consisting of three molecules, bound together through the oxygen atoms, in consequence of which no normal carbonyl shift would be present. Such a frequency is also missing in chloral hydrate (500), but is present in chloral (173, 500).

4. Esters. The esters have been investigated in considerable detail (124, 353, 444, 445, 488, 605). There is a nearly negligible change in the ester carbonyl shift caused by increasing the chain length of the ester radical. It is to be pointed out that substitutions in the ester radical are in the β-position so far as the carbon atom of the carbonyl group is concerned. Changes in substituent groups have a much more pronounced effect on the carbonyl frequency in the α-position. The effect of substitution in the α-position to the ester carbon atom may be quite marked, however, and may extend over 50 wave numbers, as shown in table 13, taken from the data of Cheng (124). This author has attempted to evaluate the characteristic frequency shifts of the substituted esters.

TABLE 13

Carbonyl frequency in esters of the type XCOOR

ESTER (XCOOR)	$\Delta\bar{\nu}$						
	X = H	X = Cl	X = CH₃	X = CH₂Br	X = CH₂Cl	X = CHCl₂	X = CCl₃
1. R = CH_3	1717	1780	1738	1740	1748	1755	1768
2. R = C_2H_5	1715	1772	1736	1738	1747	1750	1763
3. R = C_3H_7	1719	1775	1739	1736	1742	1749	1764
4. R = C_4H_9	1718	1773	1737	1732	1739	1751	1765
5. R = C_5H_{11}	1718	1774	1738		1744	1756	1769

With compounds having the radical  $\mathrm{BrCH_2C}{\scriptstyle\begin{matrix}/\!\!/ O\\ \backslash O\end{matrix}}$, these are $\Delta\bar{\nu}$ 370, 550, 670, 710, 1740, 2960; with  $\mathrm{ClCH_2C}{\scriptstyle\begin{matrix}/\!\!/ O\\ \backslash O\end{matrix}}$, $\Delta\bar{\nu}$ 410, 590, 700, 790, 1740, 2960; with  $\mathrm{Cl_2CHC}{\scriptstyle\begin{matrix}/\!\!/ O\\ \backslash O\end{matrix}}$, 230, 420, 770, 1750, 3010, and with  $\mathrm{Cl_3CC}{\scriptstyle\begin{matrix}/\!\!/ O\\ \backslash O\end{matrix}}$, 200, 290, 430, 680, 830, 1765. In figure 13 are given the Raman spectra of some esters and salts of acetic acid, taken from the data of Cheng (111). The most unique point illustrated in this figure is the lack of lines corresponding to the carbonyl frequency in the acid salts. This has been noted by Krishnamurti (376), Ghosh and Kar (248), and Hibben (313). This is not explicable on the same basis as the disappearance of the double-bond frequency, as in the allenes. Generally this has been accounted for by a type of hydration, that is, the formation of an OH group in place of a double bond, such as in the case of formaldehyde and in urea (376, 485). It has been reported (162, 163) that this frequency may be present but exceedingly weak in the acid salts. The dibasic acids present a definite problem which will be discussed shortly.

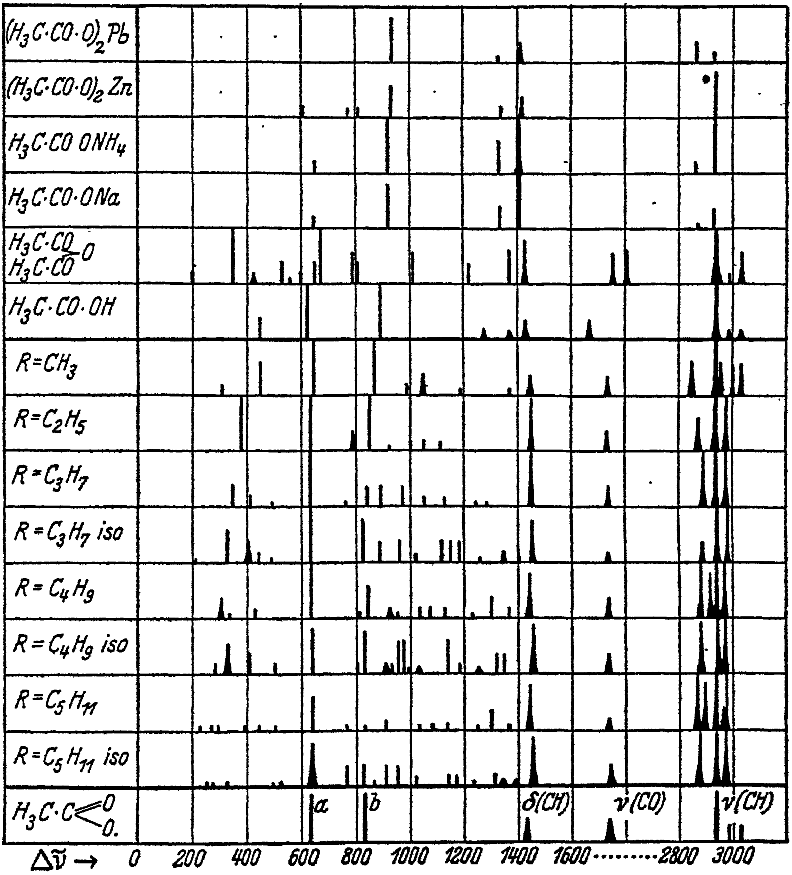


FIG. 13. The Raman spectra of acetic acid and of some of its salts and esters (after Cheng)

5. Anhydrides. While some of these compounds could be considered heterocyclic, it is believed that they may be more properly treated in connection with the carbonyl frequencies. The anhydrides have been sparingly investigated (369, 490, 592). Nevertheless, they present the unique property of having two carbonyl frequencies. The shifts observed for the aliphatic anhydrides are $\Delta\bar{\nu}$ 1754 (2) to 1745 (2) for one of the shifts, depending upon the length of the chain, and $\Delta\bar{\nu}$ 1804 (3), which remains constant, for the other shift. Both of these values are higher than observed with any other carbonyl compound with the exception of the halogen substituted ketones which may have shifts near $\Delta\bar{\nu}$ 1800. Succinic, methylsuccinic, maleic, and phthalic anhydrides yield $\Delta\bar{\nu}$ 1775 and 1845. This augmentation of the frequencies of the latter group may possibly be ascribed to the ring structure for these compounds. It may be noted, however, that both phthalid and furfural, while containing a ring oxygen adjacent to the carbonyl group, possess only one carbonyl frequency shift.

6. Polybasic acids and derivatives. The saturated polybasic acids which have been investigated are oxalic (313, 376, 536), malonic (248), tartaric (502), and citric (476). The dibasic acids have frequency shifts which may be strongly affected by their ionization and other factors. In oxalic acid there are two frequency shifts in the aqueous solution and in the anhydrous material near $\Delta\bar{\nu}$ 1650 and 1750; one of these corresponds to the normal acid shift and one is nearer the ester or anhydride frequency that that of the normal acid. Hibben (313) has observed that there is apparently some suppression of the carbonyl frequencies in oxalic acid dihydrate. This is explained on the assumption that it has a chelate structure extending throughout long chains in the crystals, but that on solution this structure breaks down, permitting at least one of the carboxyl groups to function normally. The other less ionized group functions more as an ester. In alcoholic solution there is only one carbonyl shift $\Delta\bar{\nu}$ 1755, so that both carboxyl groups must function identically in alcoholic solution. The increase in the force constant resulting from the increased carbonyl frequency is indicative of a stronger bond between the carbon and the oxygen in oxalic acid than in the other organic acids. It has been noted that a similar phenomenon results on the substitution of chlorine adjacent to the carboxyl group in the aliphatic acids with the consequent increase in strength of these acids. Apparently the proximity of one carbonyl group to another increases the Raman frequency. This is notable in the case of pyruvic acid (168, 354), which has a shift $\Delta\bar{\nu}$ 1735 (3) and a doubtful one at $\Delta\bar{\nu}$ 1769, and in malonic acid (278), which yields $\Delta\bar{\nu}$ 1737, and citric acid, which gives $\Delta\bar{\nu}$ 1730. Rao (536) attributes $\Delta\bar{\nu}$ 1430 observed in oxalic acid as due to the hydroxyl group oscillation. A shift $\Delta\bar{\nu}$ 1450 is present in all the alcohols, but is more properly ascribed to the bending moment of the hydrogen. With oxalic acid this is not a possible allocation of this frequency, since no C—H group is present. Nevertheless, there is no other evidence in support of $\Delta\bar{\nu}$ 1430 as a hydroxyl vibration. The $\Delta\bar{\nu}$ 850 and 480 observed are due to the linear chain and bending oscillations, respectively.

The salts of tartaric acid give, according to Peychès (502) but not according to Nisi (476), a frequency shift $\Delta\bar{\nu}$ 1620 or 1660 depending on the mass of the anion. The presence of this carbonyl frequency in these salts is in contradistinction to the lack of this frequency in salts of the dibasic acids, oxalic acid (313) and malonic acid (248), already mentioned.

7. *Unsaturated carbonyl compounds.* The unsaturated carbonyl compounds such as crotonyl chloride have two strong shifts $\Delta\bar{\nu}$ 1744 and 1761, —a considerable reduction over the saturated acyl halide carbonyl shifts. The same diminution is also present in ethylideneacetone (366), which has $\Delta\bar{\nu}$ 1668 for the carbonyl frequency; phorone has $\Delta\bar{\nu}$ 1668. Apparently the conjugation of the double-bond carbonyl with the double-bond ethylenic group in unsaturated compounds causes a reduction in the carbonyl frequencies of roughly 40 wave numbers. The effect on the ethylenic linkage shift, on the contrary, is rather slight, and is to increase it by a small amount.

With the unsaturated acids the usual or modified carbonyl shift is weakened to the point of extinction. There have been so few compounds, however, of this type investigated, that it is dangerous to extrapolate too far in the direction of accounting for this phenomenon. Furthermore, most of these compounds have been studied from the point of view of the ethylenic rather than the carbonyl shifts. Nevertheless, the salts of dibasic unsaturated acids like fumaric acid may possibly show a frequency shift corresponding to the carbonyl group, which is in the region $\Delta\bar{\nu}$ 1650 (603). The esters of saturated dibasic acids (171, 485) give frequency shifts at $\Delta\bar{\nu}$ 1742, which is a slightly higher value than for monobasic acids. The unsaturated esters (180, 231, 283, 366) yield $\Delta\bar{\nu}$ 1725, on the average, which is slightly less than for the saturated compounds.

There have been a few unsaturated aldehydes investigated. Here likewise there is a very marked lowering of the carbonyl frequency. This has been noted in 2-methyl-2-penten-1-al by Grédy (282) and in crotonaldehyde by Hibben (310). In both cases the shift was $\Delta\bar{\nu}$ 1689. However, if the ethylenic double bond is sufficiently removed from the carbonyl group there is no longer any interaction between them, and the carbonyl frequency becomes normal, as in the case of citronellal (86), where the shift is $\Delta\bar{\nu}$ 1719, and in undecylenaldehyde, where it is $\Delta\bar{\nu}$ 1721, as observed by Bonino and Manzoni-Ansidei (90).

H. Keto–enol isomerism

The demonstration of keto–enol isomerism by means of the Raman effect was one of its earliest applications. A number of the acetoacetates have been investigated by Milone (444), Dadieu and Kohlrausch (165), Kohlrausch and Pongratz (354, 358, 359), and Pal and Sen Gupta (485). The last-named authors early pointed out the presence of two frequencies, $\Delta\bar{\nu}$ 1656 and 1750, in the ethyl acetoacetates. On reëvaluation these are more nearly $\Delta\bar{\nu}$ 1632 and 1725. The methyl acetoacetate yields $\Delta\bar{\nu}$ 1626 and 1737; methyl methylacetoacetate yields $\Delta\bar{\nu}$ 1618, 1714, and 1734. Methyl dimethylacetoacetate shows no ethylenic shift, but yields $\Delta\bar{\nu}$ 1709 and 1738 as a doublet carbonyl frequency (358). Methyl and ethyl pyruvate have the shift $\Delta\bar{\nu}$ 1735. These shifts are in all cases relatively strong. It may be seen immediately that only those compounds which can exist in enolic form show evidence of the ethylenic linkage. Since the possibility of a migrating hydrogen ceases to exist on their substitution by methyl groups, there is no longer any evidence of C=C in the disubstituted compounds. These shifts are illustrated in figure 14 (12). The possible tautomerism of β-aminocrotonic esters has been discussed by Kohlrausch and Pongratz (358). The possibility of another type of keto-enol isomerism exists in aldol, which Hibben (310) showed has both a reduced carbonyl frequency and an ethylenic shift similar to crotonaldehyde. Crotonaldehyde, however, was not present as an impurity.

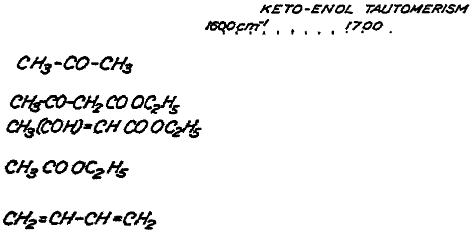
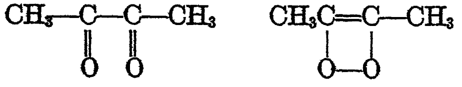


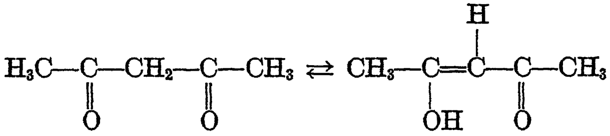
FIG. 14. The Raman shifts of the keto and enol forms of ethyl acetoacetate as compared with similar compounds (after Andrews)

Hayashi (298) has investigated the Raman spectra from diacetyl, acetylacetone, and acetonylacetone. He observed two shifts for diacetyl, $\Delta\bar{\nu}$ 1677 and 2056, in the double-bond region. The $\Delta\bar{\nu}$ 2056 has a frequency much higher than for any ketone so far observed. It is suggested that there is a type of tautomerism not involving the migration of a hydrogen atom. The $\Delta\bar{\nu}$ 1677 is attributed to the C=C in the tautomer. These two forms are indicated as follows:



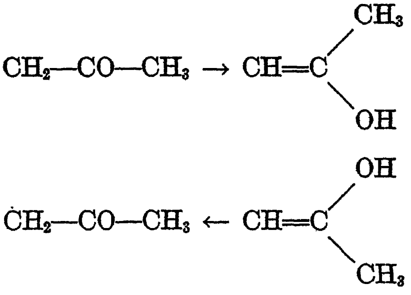
$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3 \qquad CH_3\underset{\underset{O}{|}}{C}=\underset{\underset{O}{|}}{C}-CH_3$$

These results are not compatible with those of Kohlrausch and Pongratz (358), who obtain $\Delta\bar{\nu}$ 1725 (2) for diacetyl. Hayashi pointed out that acetylacetone may be tautomeric in nature, as a stable salt is isolable from its enolic form. With this compound were observed $\Delta\bar{\nu}$ 1600 attributed to C=C, $\Delta\bar{\nu}$ 1859 for the C=O, and two frequencies $\Delta\bar{\nu}$ 3467 and 3563. These frequencies could be explained by the equilibrium between two tautomers:



$$H_3C-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 \rightleftarrows CH_3-\underset{\underset{OH}{|}}{C}=\overset{\overset{H}{|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$$

The frequency shift in the region of $\Delta\bar{\nu}$ 3500 is ascribed to the OH shift. The frequency shift $\Delta\bar{\nu}$ 1600 (8) is confirmed by Kohlrausch and Pongratz (359), who found also $\Delta\bar{\nu}$ 1655 (2) and 1723 (2) for this compound. Dimethylacetylacetone yields simply $\Delta\bar{\nu}$ 1710. The observations of Kohlrausch cannot be reconciled with those of Hayashi. Acetonylacetone yields, according to Hayashi, $\Delta\bar{\nu}$ 3670, 3613, 3272, 1710, and 1625. In these acetone derivatives only the significant shifts have been mentioned. Here the presence of two frequencies in the double-bond region is again ascribed to a tautomeric arrangement such as:



It might be mentioned that resorcinol has the double-bond frequencies $\Delta\bar{\nu}$ 1874, 1816, 1746, and 1697, despite the fact that it behaves more as a hydroxyphenol. It is suggested that there, too, tautomerism may play a rôle, leaving a ketonic group in the ring. This evidence would be more convincing if the observers had employed filtered radiation rather than an unfiltered mercury spectrum. Hayashi's results are at least interesting and by no means entirely inconsistent.

I. The Raman effect and the acetylenic linkage

The calculation of the force exerted between two carbon atoms bound by a triple bond, such as in acetylene, gives a value which is approximately three times the force between singly bound atoms. This means then that the frequency for the acetylenic grouping should occur between $\Delta\bar{\nu}$ 2100 and 2250, depending upon slight variations in the force constant. This is indeed the case, as all acetylenic compounds show a frequency shift in this region, with the exception of acetylene itself whose characteristic frequency is approximately $\Delta\bar{\nu}$ 1975. Consequently in acetylene it is probable that the force is slightly less between the carbon atoms than in its substituted products.

Numerous workers have investigated acetylene. Among these are Bhagavantam (45, 46), Daure (194, 195, 196, 197), Glockler and Davis (251), Glockler and Morrell (255), Lewis and Houston (411), Morino (455), Nisi (478), Segré (555), and Venkateswaran and Sibaiya (615). Not only is the carbon to carbon frequency exalted in acetylene but also the carbon to hydrogen frequency is increased to $\Delta\bar{\nu}$ 3320, which is one of the highest values observed for hydrogen and is exceeded only by the hydrogen in H↔O and N↔H. The acetylenic shift is quite sensitive to substitution, but in a somewhat different sense from the ethylenic frequency. In methylacetylene, for example, there is an increase in the frequency, as compared with acetylene, of 163 wave numbers, the observed value being $\Delta\bar{\nu}$ 2123 for the symmetrical oscillations in methylacetylene. In dimethylacetylene there is an additional increase of approximately 100 wave numbers or more and the appearance of a new line, the resultant shifts being $\Delta\bar{\nu}$ 2234 and 2312. The $\Delta\bar{\nu}$ 2312 shift corresponds to a completely symmetrical linear vibration and $\Delta\bar{\nu}$ 2234 to the linear asymmetrical one.

The maximum number of vibration frequencies to be expected from a molecule depends upon the number of its degrees of freedom, there being three for each atom, less six translational and rotational degrees for the molecule as a whole. Consequently the maximum number of vibrational frequencies which may be expected is 3 × the number of atoms − 6 or $(3n - 6)$. Placzek (511) has indicated that this expected maximum number of frequencies is reduced if the molecule has symmetry. Glockler and Davis (251) have analyzed the vibrations in methylacetylene and conclude that there are eleven Raman frequencies of a possible fifteen, one of which can be interpreted as an overtone. The frequency shifts for methylacetylene and the modes of oscillation which may give rise to these frequencies are indicated in table 14 (251).

As has been observed, with any of the hydrocarbons the lower frequencies are deformation oscillations. The shift $\Delta\bar{\nu}$ 929 is probably a linear vibration of a methyl group against the rest of the molecule. $\Delta\bar{\nu}$ 1382 appears in most of the acetylenes. It is doubted, however, that this can be ascribed to a hydrogen attached to a CH_2 or CH_3 group adjacent to an unsaturated carbon atom. The other lines have the significance which has been described already. Dimethylacetylene has in addition to the two strong lines already mentioned three other lines $\Delta\bar{\nu}$ 2180, 2201, and 2280, which are weak and are interpreted as rotational changes occurring with the $C\equiv C$ vibration. In vinylacetylene there is one acetylenic shift $\Delta\bar{\nu}$ 2098 and one ethylenic shift $\Delta\bar{\nu}$ 1595. The acetylenic shift is slightly lower than that for methylacetylene. The ethylenic shift is also depressed by a considerable amount from its average value.

Bourguel and Daure (102, 103) and Grédy (275, 279, 280) investigated the effect of substitution on the acetylenic linkage. Blanche Grédy has prepared and examined a large number of acetylenes and has ably discussed them in some detail (280). The effect of substitution on the acetylenes is given in table 15. This includes cyclic compounds as well as straight chain radicals, inasmuch as the acetylenic linkage never appears in a ring, as does the ethylenic linkage. In the index of compounds, however, the acetylenes are divided into the respective class compounds, that is, the aromatic derivatives of the acetylenes are under the aromatic compounds.

TABLE 14

The frequency shifts for methylacetylene and the modes of vibration which give rise to these frequencies

MODES OF VIBRATION	$\Delta\bar{\nu}$	INTENSITY
$(H_3C)\downarrow-C\uparrow\vdots C\uparrow-H\downarrow$	336	9(b)
$(H_3C)\downarrow-C\uparrow\vdots(CH)\downarrow$	643	5(b)
$(H_3C)\rightarrow-\leftarrow(C\vdots CH)$	929.5	8(s)
$H\uparrow-H_2\downarrow-(C-C\vdots C)\uparrow-H\downarrow$	1382.5	6(b)
$H\uparrow-H\downarrow-(HC-C\vdots CH)$	1448	2(b)
$(H_3C)-C\rightarrow\vdots\leftarrow C(H)$	2123.5	11(s)
$(H_3)\rightarrow-\leftarrow(C-C\vdots C)-H\rightarrow$	2867	6(s)
$(H_3)\rightarrow-\leftarrow(C-C\vdots CH)$	2926.2	10(s)
$H\rightarrow-\leftarrow(H_2C-C\vdots CH)$	2971	4(b)
$(H_3C-C\vdots C)\rightarrow-\leftarrow H$	3305	2(s)

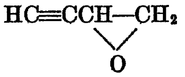
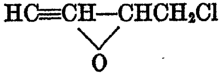
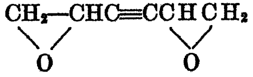
It has been mentioned that the first members of the series of "true" acetylenes ($RC\equiv CH$) have only one linear $C\equiv C$ Raman shift. This is the case for all the monosubstitution derivatives. Furthermore, this shift will fall approximately at $\Delta\bar{\nu}$ 2119, practically regardless of the length or constitution of the chain attached to the other triply bound carbon atom. The principal exceptions are acetylene itself and vinylacetylene. In the disubstituted acetylenes there is an immediate appearance of two strong lines which are, in general, constant throughout a given series. This is indicated in table 15 under section II of the hydrocarbons. For each homologous series, as in the methylacetylenes, the character of the

TABLE 15

The effect of substitution on acetylenic frequencies

			$\Delta\bar{\nu}$					
			Hydrocarbons					
I		II				III		
$CH\equiv CH$	1960 (5)	$CH_3C\equiv CCH_3$	2234 (10)		2312 (5)	$C_5H_{11}C\equiv CCH_3$	2233 (10)	2301 (5)
$CH_3C\equiv CH$	2123 (7)	$C_2H_5C\equiv CCH_3$	2238 (10)		2304 (5)	$C_5H_{11}C\equiv CC_2H_5$	2232 (8)	2293 (5)
$CH_2{=}CHC\equiv CH$	2098 (7)	$C_3H_7C\equiv CCH_3$	2238 (10)		2304 (5)	$C_5H_{11}C\equiv CC_3H_7$	2234 (7)	2293 (5)
$C_4H_9C\equiv CH$	2121 (7)	$C_4H_9C\equiv CCH_3$	2235 (10)		2303 (5)	$C_5H_{11}C\equiv CC_4H_9$	2231 (7)	2293 (5)
$(CH_3)_2CHCH_2C\equiv CH$	2118 (7)	$C_5H_{11}C\equiv CCH_3$	2233 (10)		2301 (5)	$C_6H_5C\equiv CCH_3$	2214 (10)	2253 (10)
$C_5H_{11}C\equiv CH$	2118 (7)	$C_6H_{13}C\equiv CCH_3$	2233 (10)		2303 (5)	$C_6H_5C\equiv CC_2H_5$	2210 (5)	2238 (7)
$C_6H_{13}C\equiv CH$	2119 (7)	$C_5H_9C\equiv CCH_3$	2239 (10)	2280 (1)	2320 (1)	$C_6H_5C\equiv CC_3H_7$	2210 (2)	2238 (7)
$HC\equiv C(CH_2)_5C\equiv CH$	2118 (7)	$C_5H_9CH_2C\equiv CCH_3$	2234 (10)		2302 (5)	$C_6H_{13}C\equiv CCH_3$	2233 (10)	2305 (5)
$C_5H_9C\equiv CH$	2116 (10)	$C_6H_5C\equiv CCH_3$	2214 (10)	2253 (10)		$C_6H_{13}C\equiv CC_2H_5$	2232 (70	2294 (5)
$C_5H_9CH_2C\equiv CH$	2119 (10)	$C_6H_{11}C\equiv CCH_3$	2239 (10)	2259 (2)	2316 (2)	$C_6H_{13}C\equiv CC_3H_7$	2233 (7)	2294 (2)
$C_6H_5C\equiv CH$	2111 (10)	$C_6H_{11}CH_2C\equiv CCH_3$	2235 (7)		2303 (5)	$C_6H_{13}C\equiv CC_4H_9$	2233 (7)	2294 (2)
$C_6H_5CH_2C\equiv CH$	2120 (8)							
$C_6H_{11}C\equiv CH$	2118 (7)							
$C_6H_{11}CH_2C\equiv CH$	2118 (7)							

Ethers				Alcohols			
	I				I		
$HC\equiv CCH_2OCH_3$	2118 (10)			$HC\equiv CCH_2OH$	2118 (10)		
				$HC\equiv CC(CH_3)_2OH$	2120 (8)		
	II			$C_5H_{11}C\equiv CCH_2OH$		2226 (7)	2290 (8)
$C_5H_{11}C\equiv CCH_2OCH_3$	2216 (5)	2237 (5)	2282 (8)	$C_6H_{13}C\equiv CCH_2OH$		2227 (7)	2289 (8)
$C_6H_{13}C\equiv CCH_2OCH_3$	2115 (5)	2237 (5)	2282 (8)	$C_5H_9CH_2C\equiv CCH_2OH$		2227 (10)	2289 (8)
$C_5H_9CH_2C\equiv CCH_2OCH_3$	2216 (5)	2235 (5)	2282 (8)	$C_6H_{11}CH_2C\equiv CCH_2OH$		2228 (7)	2290 (8)
$C_6H_{11}CH_2C\equiv CCH_2OCH_3$	2217 (5)	2234 (5)	2281 (8)	$C_6H_5C\equiv CCH_2OH$	2198 (2)	2239 (10)	
$C_6H_5C\equiv CCH_2OCH_3$	2200 (5)	2240 (10)					

III		
$C_5H_{11}C{\equiv}CCH(OCH_3)CH_3$	2240 (10)	2308 (1)
$C_5H_9CH_2C{\equiv}CCH(OCH_3)CH_3$	2239 (7)	2304 (1)
$C_6H_{11}CH_2C{\equiv}CCH(OCH_3)CH_3$	2241 (10)	2307 (1)
$C_6H_5C{\equiv}CCH(OCH_3)CH_3$	2221 (10)	2241 (10)
IV		
$C_5H_{11}C{\equiv}CC(CH_3)_2OCH_3$	2236 (10)	
$C_5H_{11}C{\equiv}CC(CH_3)(C_2H_5)OCH_3$	2236 (10)	
$C_6H_{11}CH_2C{\equiv}CC(CH_3)_2OCH_3$	2234 (10)	
$C_6H_5C{\equiv}CC(CH_3)_2OCH_3$	2215 (7)	2238 (10)
V		
 $\underset{\diagdown O \diagup}{HC{\equiv}CCH{-}CH_2}$	2126 (7)	
 $\underset{\diagdown O \diagup}{HC{\equiv}CH{-}CHCH_2Cl}$	2138 (7)	
 $\underset{\diagdown O \diagup}{CH_2{-}CH}C{\equiv}C\underset{\diagdown O \diagup}{CHCH_2}$	2253 (5)	
Esters		
$C_5H_{11}C{\equiv}CCOOCH_3$	2238 (10)	
$C_6H_{13}C{\equiv}CCOOCH_3$	2238 (10)	

II		
$C_5H_{11}C{\equiv}CCHOHCH_3$	2250 (8)	2312 (1)
$C_6H_{13}C{\equiv}CCHOHCH_3$	2250 (10)	2310 (1)
$C_5H_9CH_2C{\equiv}CCHOHCH_3$	2249 (10)	2303 (1)
$C_6H_{11}C{\equiv}CCHOHCH_3$	2237 (8)	incomplete
$C_6H_{11}CH_2C{\equiv}CCHOHCH_3$	2250 (10)	2314 (1)
$C_6H_5C{\equiv}CCHOHCH_3$	2233 (10)	
III		
$C_5H_{11}C{\equiv}CC(CH_3)_2OH$	2239 (10)	
$C_5H_{11}C{\equiv}CCOH(CH_3)C_2H_5$	2238 (10)	
$C_6H_{11}CH_2C{\equiv}CC(CH_3)_2OH$	2237 (10)	
$C_6H_5C{\equiv}CC(CH_3)_2OH$	2230 (10)	
$(C_5H_{11}C{\equiv}C)_2CHOH$	2250 (7)	2304 (1)
$(C_5H_{11}C{\equiv}C)_3COH$	2236 (7)	
Halogen derivatives		
$CI{\equiv}CI$	2109 (8)	
$C_6H_5C{\equiv}CCl$	2225 (10)	

substitution on the other acetylenic carbon does not change in general the magnitudes of the shifts. There is, however, one exception, and that is the substitution of a phenyl group. In the true acetylenes this substitution has a slight effect. In the methylacetylenes the shift whose average frequency is $\Delta\bar{\nu}$ 2236 is reduced to $\Delta\bar{\nu}$ 2214 by phenyl substitution, and the shift whose average is $\Delta\bar{\nu}$ 2304 is reduced to $\Delta\bar{\nu}$ 2253 with a concomitant marked increase in its intensity. Substitution with cyclohexane causes the appearance of a weak line at $\Delta\bar{\nu}$ 2259. Under section III of the hydrocarbons is shown the effect of increasing the mass of one substituent group while holding constant the mass of the other substituent group. This demonstrates that as both substituent groups are increased in mass there is relatively little change in the frequency shifts beyond the initial marked effect caused by substituting a more complex group for a single hydrogen. Following the initial effect of substituting a phenyl group on one of the acetylenic carbons, it is evident that increasing the mass of the second substituent beyond that of a methyl group does not seriously alter the frequency shifts.

On considering next the changes which may take place when a carbinol group is substituted for a hydrocarbon group it is apparent that in the true acetylenes there is little effect, the average shift being $\Delta\bar{\nu}$ 2119. This is shown under section I of the alcohols. Furthermore, on disubstitution there is a similar appearance of two strong frequencies corresponding fairly closely to those observed in the methylacetylenes. There is an apparent decrease, however, of approximately 10 wave numbers in the larger of the two frequency shifts. If the phenyl group is one of the substituents, in place of $\Delta\bar{\nu}$ 2253 present in methylphenylacetylene there appears a weak frequency at $\Delta\bar{\nu}$ 2198.

However, if the substituent carbinol group represents a secondary alcohol of the general form $R—C{\equiv}C—CHOHCH_3$, as shown under section II of the alcohols, then there is approximately an increase of 20 wave numbers in both observed acetylenic frequencies. Here again the phenyl group causes a different effect from the other radicals represented by R. It gives rise to only one Raman frequency, $\Delta\bar{\nu}$ 2233. If the alcohol substitution is represented by $R—C{\equiv}CC(CH_3)_2OH$, then in place of two characteristic frequency shifts there is only one, $\Delta\bar{\nu}$ 2238, which appears very strong. This behavior is quite remarkable in contrast to the effect of substitution so far presented.

The monosubstituted ethers are practically identical with the other monosubstituted derivatives. In the compounds of the form $RC{\equiv}C\text{-}CH_2OCH_3$ there are three $C{\equiv}C$ frequency shifts, $\Delta\bar{\nu}$ 2216, 2237, and 2282. These shifts remain constant throughout the normal series except for the usual influence of the phenyl radical, which eliminates the highest

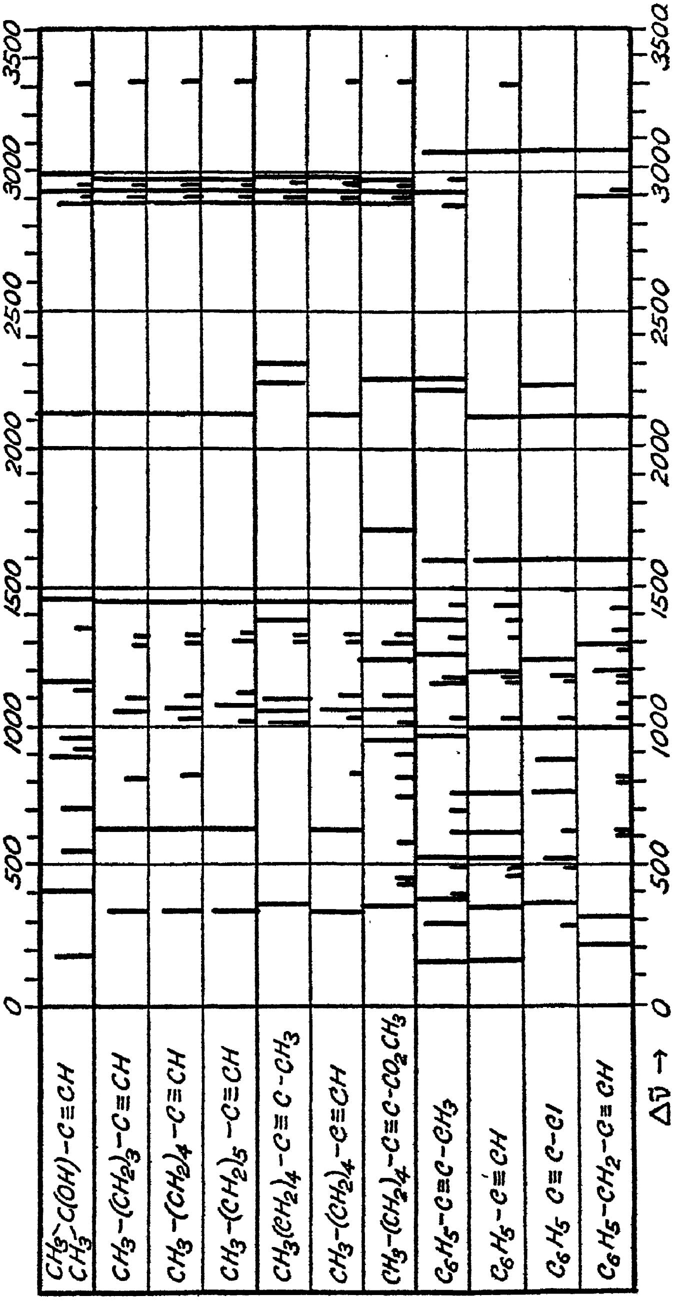


FIG. 15. The Raman spectra of some acetylenic compounds (after Bourguel and Daure)

frequency and slightly diminishes the lowest frequency shift. The secondary ethers as indicated under section III of the ethers have only two shifts, one of which is of approximately the same magnitude as the medium frequency shift in the normal ether, and the other considerably larger than the highest frequency shift of the normal ethers. The tertiary ethers have one strong shift at $\Delta\bar{\nu}$ 2235 with the exception of the phenyl derivative, which in this case has two shifts instead of one, namely, $\Delta\bar{\nu}$ 2215 and 2238. The decrease in the number of characteristic frequencies in going from the normal to the tertiary derivatives somewhat parallels the behavior with the alcohols. The epoxy derivatives of normal acetylene give a frequency close to that observed with other similar acetylenes.

These figures demonstrate in a clear-cut fashion the very definite influence of the substitution on characteristic frequency shifts. Nevertheless, in the acetylenic compounds the displacement attributed to this linkage is not the only criterion of identification. Bourguel and Daure (102) and Grédy (280) have pointed out that other frequencies are also quite characteristic in the normal acetylenes. The $\Delta\bar{\nu}$ 340 is generally present in the normal, and $\Delta\bar{\nu}$ 375 and 1380 in the disubstituted compounds. They are almost equally characteristic frequencies. In figure 15 are given the complete Raman spectra for a typical group of these compounds.

J. The Raman spectra of cyclic compounds

The simplest of the cyclic compounds are the cyclopropanes. The Raman spectra of cyclopropane and some of its derivatives have been determined by Lespieau, Bourguel, and Wakeman (407, 408). Cyclopropane can be considered a system of three masses substituted on the corners of a triangle. By assuming equal force and an equilateral triangle Yates (668) calculated the probable frequencies as being $\Delta\bar{\nu}$ 400 and 1350. The observed frequencies, however, follow more closely the calculations of Bhagavantam (36), where the ratios of the principal C—C frequencies are as $\sqrt{2}$. This follows from the fact that the normal frequencies of a system of type X_3 are given by

$$\Delta\bar{\nu}_1 = k\sqrt{\frac{3F}{2M}} \qquad \text{and} \qquad \Delta\bar{\nu}_2 = k\sqrt{\frac{3F}{M}}$$

Since it may be assumed, as a first approximation, that F and M remain constant, then

$$\Delta\bar{\nu}_2 = \Delta\bar{\nu}_1\sqrt{2}$$

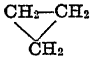
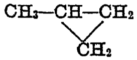
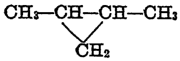
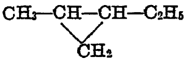
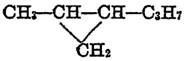
This gives a calculated value for the two frequencies of $\Delta\bar{\nu}$ 1212 and 858 on the assumption that the C—C frequency in ethane $\Delta\bar{\nu}$ 990 may be applied in this connection. The observed values are $\Delta\bar{\nu}$ 1188 and 867, respectively, which are in moderate agreement.

In table 16 are given the principal Raman shifts of the cyclopropanes. Some of the very weak lines are omitted. Lespieau, Bourguel, and Wakeman postulated that there is a frequency varying from $\Delta\bar{\nu}$ 1188 to 1214, which remains fairly constant throughout the series. On the other hand another characteristic frequency varies progressively with the number of carbon atoms in the molecule. This changes from $\Delta\bar{\nu}$ 1188 in cyclopropane to $\Delta\bar{\nu}$ 982 in methylcyclopropane, $\Delta\nu$ 915 in dimethylcyclopropane, $\Delta\bar{\nu}$ 813 in methylethylcyclopropane, and $\Delta\bar{\nu}$ 760 in methylpropylcyclopropane. These changes follow the equation

TABLE 16

The Raman spectra of some cyclopropanes

$\Delta\bar{\nu}$

 $CH_2—CH_2$, CH_2	 $CH_3—CH—CH_2$, CH_2	 $CH_3—CH—CH—CH_3$, CH_2	 $CH_3—CH—CH—C_2H_5$, CH_2	 $CH_3—CH—CH—C_3H_7$, CH_2
			737(5)	
		746(5)	746(8)	
	759(5)	765(8)	756(5)	760(8)
		783(5)	783(1)	786(5)
			813(8)	825(1)
867(5)	851(5)	866(1)	869(5)	861(1)
			889(5)	
		915(7)		
	892(7)		967(1)	967(5)
		1035(1)	1043(1)	1035(8)
1188(10)		1173(1)	1172(5)	1172(1)
	1207(7)	1214(7)	1209(8)	1207(7)
			1221(5)	1221(5)
1439(1)	1462(1)	1455(7)	1305(1)	1455(7)
				2850(5)
	2874(5)	2875(7)	2870(7)	2876(7)
				2906(7)
			2912(7)	
	2931(5)	2933(7)	2937(7)	2937(7)
	2957(5)	2954(7)		2963(7)
			2966(7)	
		2983(5)		
3011(7)	2998(7)	2999(10)	2999(10)	3000(10)
3029(7)				
3076(1)	3074(1)	3064(5)	3066(7)	3065(7)

$$\Delta\bar{\nu} = 1188 \sqrt{\frac{3}{n}}$$

where n is the number of carbon atoms in the molecule. This is shown in figure 16 where the calculated values are indicated by dotted lines. The intent of the authors is somewhat obscured by errors in printing. Nevertheless, it is clear that a frequency appears near $\Delta\bar{\nu}$ 3065 to 3074 which does not occur in the aliphatic hydrocarbons. This occurs in other cyclic compounds such as cyclopentene, benzene, and cyclohexadiene. It apparently is not present, however, in cyclopentane, cycloheptane, cyclooctane and derivatives, but may occur in cyclohexene. It is a disputed point that this frequency is characteristic of the ring linkage in the larger rings or primarily characteristic of unsaturation. In any case the $\Delta\bar{\nu}$ 3000 and approximately 3070 are quite characteristic of the cyclopropane C—H vibration. There is no accounting for the absence of a shift near $\Delta\bar{\nu}$ 1450 in the methylethylcyclopropane. Apparently the band at $\Delta\bar{\nu}$ 3070, which is feeble in cyclopropane, readily increases in intensity with substitution until it becomes nearly as strong as the band at $\Delta\bar{\nu}$ 3000. The relatively strong shift at $\Delta\bar{\nu}$ 3029 in cyclopropane disappears on further substitution. Canals, Godchot, and Cauquil (118) and Weiler (634, 635, 636) have investigated cyclopropane. The first-named authors have also studied other cyclic compounds. These results are given in table 17. It is presumed (118) that $\Delta\bar{\nu}$ 1188, 1290, 1268, and 1293 are frequency shifts characteristic of a five-carbon nucleus. This is partially confirmed by Grédy (289) in her extensive studies. The shifts she gives, however, are $\Delta\bar{\nu}$ 890, 1020, 1224, 1305 on the average. The shifts characteristic of the cyclohexane nucleus (259) are $\Delta\bar{\nu}$ 440, 801, 1029, 1165, 1268. This is also confirmed by Grédy (280) with, however, $\Delta\bar{\nu}$ 788 considered as the first identifying shift. In the ethylenic derivatives of cyclopentane observed

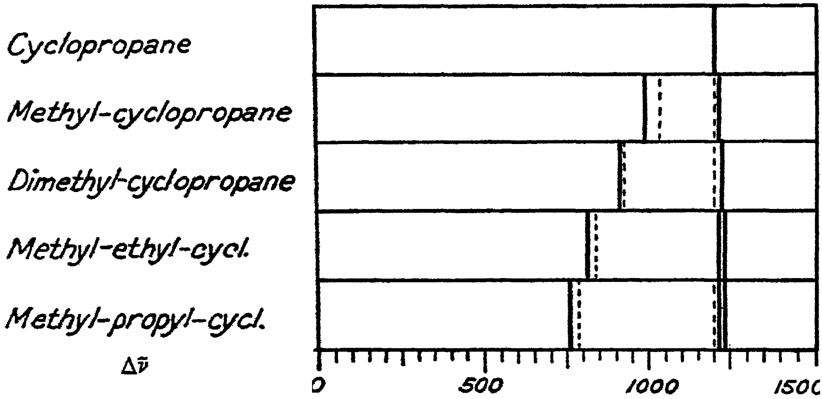


FIG. 16. The alteration of one of the principal lines in the Raman spectrum of cyclopropane as a function of substitution (after Lespieau, Bourquel, and Wakeman)

by Piaux (508) it is presumed that $\Delta\bar{\nu}$ 890 is characteristic of the saturated cyclopentyl group. In these unsaturated derivatives, shifts appear near $\Delta\bar{\nu}$ 3000 and 3070, which substantiate the general observation that shifts in this region are attributable to the unsaturated C—H linkage. With the cyclohexanes there exists a possibility of *cis-trans* isomerism. This has been carefully studied by Miller and Piaux (440, 441) and by Miller and Lecomte (439) and the results are indicated in table 18 for the dimethylcyclohexanes. While these show extraordinary similarity there are, nevertheless, notable differences which would enable their being distinguished from each other. The presumption that $\Delta\bar{\nu}$ 1164 and 1355 are characteristic shifts of the *trans*-form and $\Delta\bar{\nu}$ 1260 and 1053 of the *cis*-form (472) is not particularly tenable. Hayashi (302) and Nevgi and Jatkar (472) have also investigated the cyclohexanes and cyclohexenes. The C—H bond appears in the cyclohexanes in much the same position as the aliphatic C—H. In general $\Delta\bar{\nu}$ 600 to 1300 are identified with C—C bonds and $\Delta\bar{\nu}$ 200 to 600 with C—C—C bonds.

TABLE 17

The Raman spectra of some saturated cyclic compounds

$\Delta\bar{\nu}$						
Cyclopentane	Methylcyclopentane	Cyclohexane	Cycloheptane	Methylcycloheptane	Cycloöctane	Methylcyclooctane
		379	335	320	243	
301						
	523	425	397	381	371	
889	845	801	729	722	700	703
	890					
1032		1029	1005	1000	988	996
1205	1205	1165	1165	1177	1171	1159
1290	1299	1268	1282	1278	1293	1286
1370	1374	1346	1345	1351	1367	1347
1450	1458	1440	1439	1444	1439	1452
2873	2873	2854	2858	2855	2857	2864
2942	2942	2926	2903	2922	2914	2904
2973	2974	2933	2933	2945	2939	2927–2954

The oxygenated derivatives such as the cyclohexanols have been studied by Piaux (504) and by Nevgi and Jatkar (472). The latter authors postulate $\Delta\bar{\nu}$ 798 to 779 as characteristic of the alcoholic grouping. The change in position of the substituent as in *o*-, *m*-, and *p*-methylcyclohexanol results in a progressive increase in the frequencies $\Delta\bar{\nu}$ 443, 457, 482, and $\Delta\bar{\nu}$ 522, 551, and 649, respectively. In *o*-, *m*-, and *p*-methylcyclohexanones these

TABLE 18

Raman spectra of some isomeric cyclohexanes

1,2-Dimethylcyclohexane		1,3-Dimethylcyclohexane		1,4-Dimethylcyclohexane	
trans	*cis*	*trans*	*cis*	*trans*	*cis*
		253(1)			
	333(2)				
			353(1)		
			373(2)	374(5)	372(5)
		407(5)			
415(5)	414(5)	420(8)			
440(5)		446(2)	453(2)	452(5)	463(2)
498(7)			487(1)	473(2)	474(5)
	537(5)	545(8)			
	593(2)				
			625(2)		637(5)
				701(1)	702(1)
749(7)	730(7)	771(7)	752(7)	760(7)	760(7)
				784(1)	787(5)
819(5)			802(1)		
857(5)	842(8)	847(5)	861(2)		
	920(2)	935(1)	937(2)	927(1)	
950(5)	944(5)	956(1)		951(2)	954(5)
	977(8)	991(2)	980(2)		976(2)
1005(8)	1005(8)		1009(2)	1005(1)	1000(5)
	1053(5)	1058(7)	1055(8)	1061(7)	1055(8)
1078(5)			1074(1)		
	1095(8)		1100(2)		1099(5)
		1113(2)			
1164(8)	1159(5)	1165(5)	1163(8)	1163(5)	1163(5)
		1181(5)		1183(5)	
1218(8)	1221(5)	1219(5)	1212(5)		1206(5)
1252(5)	1256(8)			1247(8)	1244(2)
		1269(5)	1266(8)		1263(8)
1292(5)	1302(8)	1303(2)	1305(2)	1307(5)	1301(2)
					1318(1)
1343(8)	1320(8)	1339(5)	1327(1)	1346(8)	1343(8)
1355(8)		1355(2)	1364(1)	1361(2)	
1446(7)	1441(7)	1441(5)	1440(8)	1432(8)	1439(8)
1460(7)	1455(5)	1460(5)	1460(8)	1456(7)	1462(7)
2660(5)					
2844(7)		2845(7)	2846(7)	2848(7)	2853(10)
2854(7)	2854(10)				
	2873(8)	2870(1)	2870(7)	2868(7)	2873(8)
	2894(8)		2883(8)		2898(7)
2915(7)		2912(5)	2912(8)	2907(5)	2913(8)
2931(10)	2927(10)	2929(7)	2928(7)	2926(7)	2930(7)
2950(5)	2959(5)	2955(7)	2960(7)	2952(8)	2960(7)
2975(5)	2973(5)				

are respectively $\Delta\bar{\nu}$ 312, 410, 500, and $\Delta\bar{\nu}$ 577, 641, 692. The C=O shift in the cyclohexanones is $\Delta\bar{\nu}$ 1712 and does not vary with the position of the alkyl radical in the substituted cyclohexanones (504). In the esters, cyclohexyl acetate and cyclohexyl propionate, the C=O frequency is $\Delta\bar{\nu}$ 1742 and 1733, respectively, and is nearly identical in all cases with the aliphatic carbonyl shift (472).

In the cyclopentyl oxygenated compounds, according to Piaux (504), the C=O shift is for cyclopentanone $\Delta\bar{\nu}$ 1726 (8), 1746 (8); for 2-methylcyclopentanone $\Delta\bar{\nu}$ 1735; and for 3-methylcyclopentanone $\Delta\bar{\nu}$ 1744. These values are slightly higher than in the corresponding cyclohexane derivatives. There is no evidence of keto–enol isomerism. The presence of two carbonyl shifts in cyclopentanone is anomalous.

K. The Raman spectra of cycloölefins

The simplest cycloölefin so far investigated is cyclopentadiene. This is not only a cyclic compound but it also contains a conjugate double-bond system. Truchet and Chapron (601) obtained $\Delta\bar{\nu}$ 945 (4), 993 (3), 1109 (5), 1364 (4), 1441 (3), 1500 (5), 2870 (3), 3095 (3) as the principal lines. For the polymeric dicyclopentadienes were observed $\Delta\bar{\nu}$ 675 (3), 774 (3), 946 (3), 954 (3), 1124 (3), 1137 (3), 1439 (3), 1574 (4), 1614 (4), 2069 (2), 3058 (2). The particular feature in connection with cyclopentadiene is the shift $\Delta\bar{\nu}$ 1500 attributable to the ethylenic linkage. While this extraordinary decrease is not analogous to that observed with the allenes, it is much lower than observed in other unsaturated cyclic hydrocarbons. Godchot, Canals, and Cauquil (259, 260, 261) have investigated a series of cycloölefins, and Piaux (505, 506, 507, 508) and Weiler (636) have investigated cyclopentene and its derivatives in particular. In table 19 are given the principal Raman lines of cyclopentene and four of its hydrocarbon derivatives based on the data of Piaux, Godchot, Canals, and Cauquil. It is noticeable that the C=C shift in cyclopentene, namely $\Delta\bar{\nu}$ 1615, is approximately 27 wave numbers lower than the average ethylenic shift in the aliphatic hydrocarbons of the type R—CH=CH$_2$ as given in table 10. With substitution on the carbon atom adjacent to the double bond in cyclopentene the frequency is increased to $\Delta\bar{\nu}$ 1658, a value more comparable with the ethylenic shift obtained in compounds of the type R—CH=CH—R′. If the substituent is a phenyl radical the augmentation in the double bond shift as compared with cyclopentene is less marked, becoming $\Delta\bar{\nu}$ 1627, but if the phenyl radical is one carbon atom removed from the ethylenic group, as in benzyl-Δ^1-cyclopentene, the shift is $\Delta\bar{\nu}$ 1652. In other words, the effect of the phenyl radical does not persist through an intermediate carbon atom. The hydrogen to carbon shift in unsaturated aliphatic compounds, it will be remembered, was

$\Delta\bar{\nu}$ 3005 and 3080, as given in table 7. This type of hydrogen frequency appears strongly in all the cyclopentenes at about $\Delta\bar{\nu}$ 3055.

The principal shifts of the oxygenated derivatives of the cyclopentenes are as follows: for Δ^1-cyclopentenylcarbinol (505, 508), $\Delta\bar{\nu}$ 420 (5), 870 (5), 888 (8), 983 (5), 1022 (5), 1202 (8), 1296 (5), 1443 (7), 1466 (5), 1656 (7), 2848 (10), 2902 (10), 2952 (10), 3048 (5); for Δ^1-cyclopentenylethanol (505, 508), $\Delta\bar{\nu}$ 329 (5), 506 (5), 853 (7), 893 (7), 948 (8), 1006 (5), 1026 (5), 1079 (5), 1160 (5), 1207 (8), 1294 (5), 1444 (10), 1468 (8), 1651 (10),

TABLE 19

The Raman spectra of cyclopentene and some of its derivatives

		$\Delta\bar{\nu}$		
Cyclopentene	1-Methylcyclopentene	1-Ethylcyclopentene	1-Phenylcyclopentene	Benzylcyclopentene
				210(8)
				231(5)
	325(5)	336(5)	339(5)	
385		404		
	578(8)		619(5)	622(5)
	851(5)			
	881(8)	867		
900(8)	903(5)	906	958(5)	968(5)
964(8)		949	982(5)	
	1008(8)	993	1004(7)	1003(10)
1025(5)	1026(5)	1031(7)	1033(5)	1030(8)
1108(7)		1131		
			1157(5)	1155(5)
			1184(5)	1181(5)
1207(5)	1207(8)	1200(5)	1208(7)	1205(5)
	1259(5)			
1296(5)	1295(5)		1296(8)	
	1333(8)		1342(5)	
	1383(8)	1385		
1441(7)	1439(10)		1442(8)	1441(7)
		1445(8)		
1467(5)	1465(8)		1495(8)	1466(5)
1615(7)		1660(10)	1600(10)	1603(10)
	1658(10)		1627(10)	1652(10)
2857(7)	2848(10)	2844(8)	2845(7)	2846(7)
2878(5)		2858(5)		
2913(7)	2910(10)		2897(8)	2902(7)
			2926(8)	
2953(7)	2959(8)	2966(7)	2955(8)	2960(7)
				3037(8)
3060(7)	3045(8)	Incomplete	3061(10)	3060(8)

TAB 20

	Cha		*ub*	*-cycl*		R		
H.	899(4	3)	07(2	.296(1	441(7	467(2	.615(6	60(3
CH_3	903(4	3)	07(5	.295(1	9(8	465(5	.658(6	3 45(2
C_6H_5....	908(2	(10	08(6	.296(4	2(6	.462(1	.627(8	61)(
CH_2C_6H	902(1	(10	05(2	.297(3	.441(7	2	652(8	37(3
CH_2OH.....	888(8	2)	02(6	296(3	3(8	3	.656(8	3 48(4
CH_2OCOCH	907(4	3)	06(3	.296(1	3(8	6(6	.658(8	58(3
$CHOHCH_3$..	893(1	1)	07(4	.294(2	4(8	8(5	.651(8	51(3
$CHOHC_2H_5$.	895(7	2)	06(2	2	1(8	4(5	.650(7	3052(2
CH_2Br..			05(2		0(7		.640(7	
CHO.	882(3		05(1	---- 2	34(7		.616(9	Broad
COOCH	903(3	2)	06(2	297(3	7(9	9(4	.631(8	3072(7
CN	896(7	2)	10(3	3	7(9	8(4	.615(8	3076(8

2848 (10), 2901 (10), 2956 (8), 2978 (10), 3051 (8); for Δ^1-cyclopentenylpropanol (505, 508), $\Delta\bar{\nu}$ 854 (5), 895 (8), 950 (8), 1029 (5), 1206 (5) 1229 (5), 1441 (7), 1464 (8), 1650 (7), 2848 (7), 2876 (5), 2908 (7), 2937 (7), 2965 (8), 3052 (5); for Δ^1-cyclopentenealdehyde (508), $\Delta\bar{\nu}$ 381 (5), 480 (8), 882 (5), 954 (8), 1158 (5), 1289 (5), 1383 (8), 1434 (8), 1616 (10), 1676 (10); for methyl-Δ^1-cyclopentenylcarboxylate (508), $\Delta\bar{\nu}$ 378 (5), 870 (5), 903 (5), 946 (5), 967 (5), 1206 (5), 1297 (5), 1437 (7), 1469 (5), 1631 (7), 1715 (7), 2844 (7), 2894 (8), 2915 (8), 2954 (10), 3072 (8); and for 1-cyano-Δ^1-cyclopentene (505, 508), $\Delta\bar{\nu}$ 175 (7), 505 (5), 866 (8), 896 (8), 953 (7), 1020 (5), 1139 (5), 1210 (5), 1257 (5), 1299 (5), 1325 (5), 1437 (7), 1468 (5), 1615 (10), 2218 (10), 2848 (5), 2868 (5), 2950 (10), 3076 (8). Shifts weaker than (5) have not been included in this tabulation. The effects of different substituent groups on the characteristic frequency shifts for cyclopentene are given in table 20 from the data of Piaux (508). The modifications in the ethylenic shift for cyclopentene show approximately the same relative order as those observed by Bourguel for the modifications of this shift in the aliphatic ethylenes, which were indicated in tables 7 and 10. In the cyclic compounds, however, these modifications are more pronounced. This is particularly noticeable toward the extremes of the two respective series. The radicals generally considered negative, such as the acid, ester, and aldehyde groups, have a tendency to decrease the frequency. On the other hand, the radicals considered positive, such as alkyl groups, increase the frequency. This is only a rough approximation, however.

Like most first members of a homologous series, cyclohexene has received considerable attention. It and its derivatives have been examined by Andant (6, 7, 8), Godchot, Canals, and Cauquil (260, 261), Hayashi (302), Lespieau and Bourguel (404, 405), Morris (456), Nevgi and Jatkar (472), Weiler (634, 635, 636), and Wood and Collins (661). Unlike the ethylenic shift in cyclopentene, this shift in cyclohexene is in its average position and is found at $\Delta\bar{\nu}$ 1650. The C—H shift of the cyclic hydrocarbons, which appears near $\Delta\bar{\nu}$ 3060 in cyclopentene and benzene, is reduced to $\Delta\bar{\nu}$ 3024 (6) in cyclohexene. This shift was not recorded by Godchot, Canals, and Cauquil for this compound or with the other members of the homologous series, although it is possible that it is present. This weakening may be for reasons of symmetry. The shifts observed for a series of cyclohexenes are indicated in table 21. No notation is given as to the relative intensities. It is noted that the position of the double bond in the ring influences the ethylenic shift, as indicated in 1-methyl-Δ^3-cyclohexene. This is compatible with the already established principles indicating that the greater the distance the double bond is from a substituent group, the less effect this group has. While the other cyclohexenes have a frequency displacement between $\Delta\bar{\nu}$ 1650 and 1680, cyclooctene shows an unusual anomaly in having this frequency at $\Delta\bar{\nu}$ 1604, which is not far removed from that of cyclopentene. This may indicate a weakening of the bond in rings of five or eight carbon atoms as compared with the six- or seven-membered rings.

TABLE 21

Raman spectra of some cycloölefins

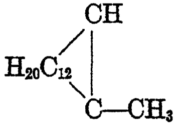
Cyclohexene	1-Methylcyclohexene	1-Methylcyclohexene	1-Ethylcyclohexene	1,4-Dimethyl-Δ^1-cyclohexene	Cycloheptene	1-Methylcycloheptene	Cyclooctene
176	132	145			144		158
273					212		243
					315	305	294
396	437	392		398		386	
451	495	447	439	417			
494	588	495		447			424
	618		625	525		603	
	695			658			
703	758	732	752	757	738	722	695
825	821	791	835	786		796	
		894	852	801			
	859	957	894	894			
997	990	995	993	996	996	996	996
1069	1069		1055		1043	1082	1096
	1087			1095		1120	
1139	1152	1229		1171		1196	1171
1220							
1272	1266	1258	1213	1256	1273	1258	1271
	1309		1381	1295		1323	
	1367				1348	1379	
1431	1445	1443 1450	1432	1443 1449	1445	1445	1439
1650	1675	1650	1675	1680	1651	1672	1604
2821							
2868	2876	2803	2817	2807	2867	2861	2864
2914	2914	2914					
2940	2940	2944	2926	2872	2912		2912
	2964	2967	2942	2944	2944	2940	2950
						2966	
3024							

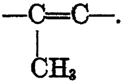
There have been two cyclohexadienes investigated. These are 1,3-cyclohexadiene, examined by Andant (8), Bonino and Manzoni-Ansidei (90, 92), Kohlrausch and Seka (370), and Murray (461), and 1,4-cyclohexadiene, which has been studied by Andant (8) and Kohlrausch and Seka (370). The spectrum for the 1,3-compound, according to Murray, is: $\Delta\bar{\nu}$ 298 (4), 394 (2), 458 (1), 505 (0), 559 (1), 618 (1), 823 (10), 848 (8), 945 (4b), 992 (15), 1060 (2), 1174 (4), 1220 (3), 1240 (2), 1266 (1), 1324 (1), 1411 (1), 1432 (5), 1576 (20), 1615 (3), 2823 (8b), 2864 (8b), 2908 (4), 2936 (8), 3018 (5), 3041 (10), 3056 (7). There are obviously two bonds distinctly ethylenic in character, corresponding to $\Delta\bar{\nu}$ 1576 and 1615. The first of these is exceedingly low for this type of frequency displacement, but it is not so low as that observed for cyclopentadiene, namely $\Delta\bar{\nu}$ 1500. The larger displacement is more comparable to that observed in benzene than that yielded by cyclohexene. Most of the strong lines in benzene have a counterpart in 1,3-cyclohexadiene. In 1,4-cyclohexadiene the strongest shift is practically identical with that of the 1, 3-compound. The other ethylenic shift is $\Delta\bar{\nu}$ 1635, and like $\Delta\bar{\nu}$ 1615 is relatively very weak. Both compounds show a strong displacement corresponding to the linear hydrogen to carbon oscillation at $\Delta\bar{\nu}$ 3040.

The oxygenated derivatives of cyclohexene have been investigated by Piaux (508) and Guillemont (288). The principal shifts observed for these compounds are as follows: 1-methyl-Δ^1-cyclohexen-6-ol (508), $\Delta\bar{\nu}$ 343 (5), 432 (5), 474 (5), 584 (5), 637 (5), 747 (5), 790 (5), 855 (5), 875 (5), 1005 (5), 1015 (5), 1035 (5), 1062 (5), 1186 (5), 1255 (5), 1312 (5), 1379 (5), 1436 (7), 1457 (8), 1670 (7), 2837 (7), 2872 (7), 2914 (7), 2943 (7); 1-ethyl-Δ^1-cyclohexen-6-ol (288), $\Delta\bar{\nu}$ 707 (5), 793 (5), 849 (5), 918 (5), 1051 (7), 1080 (5), 1102 (5), 1183 (5), 1253 (7), 1271 (7), 1300 (5), 1347 (5), 1433 (10), 1451 (7), 1667 (10); 1-methyl-Δ^1-cyclohexen-6-one (508), $\Delta\bar{\nu}$ 472 (5), 710 (5), 1023 (5), 1083 (5), 1175 (5), 1360 (8), 1434 (7), 1456 (5), 1640 (7), 1670 (7), 2878 (8), 2924 (8), 2950 (8); 1-ethyl-Δ^1-cyclohexen-6-one (288), $\Delta\bar{\nu}$ 879 (5), 1057 (5), 1093 (5), 1175 (5), 2448 (5), 1380 (5), 1434 (7), 1460 (5), 1636 (10), 1670 (10); 1-methyl-6-ethoxy-Δ^1-cyclohexene (508), $\Delta\bar{\nu}$ 1254 (5), 1306 (5), 1372 (8), 1437 (7), 1450 (8), 1673 (7), 2837 (8), 2872 (7), 2912 (7), 2936 (7); and 1-ethyl-Δ^1-cyclohexen-6-ol acetate (288), $\Delta\bar{\nu}$ 851 (7), 921 (7), 1065 (5), 1188 (5), 1254 (5), 1302 (5), 1332 (5), 1381 (5), 1434 (10), 1448 (10), 1672 (10), 1737 (5). The figures tabulated are only for the stronger shifts. In many cases, however, the C—H displacements were not determined.

The ethylenic bond in the Δ^1-substituted cyclohexenes gives $\Delta\bar{\nu}$ 1670 for the hydrocarbons, $\Delta\bar{\nu}$ 1668 for the alcohol, $\Delta\bar{\nu}$ 1638 for the ketone, $\Delta\bar{\nu}$ 1673 for the ether, and $\Delta\bar{\nu}$ 1672 for the ester derivatives, all of which are larger than the corresponding shifts in cyclopentene derivatives. In some of these oxygenated derivatives may be noted the effect of the conjugation of the C═C on the C═O vibration. It will be recalled that the aliphatic aldehydes, ketones, and esters gave $\Delta\bar{\nu}$ 1720, 1705, and 1735 respectively for the average C=O shift as shown in table 12. But in Δ^1-cyclopentenealdehyde the shift has become $\Delta\bar{\nu}$ 1676 instead of $\Delta\bar{\nu}$ 1720 and in methyl-Δ^1-cyclopentenecarboxylate $\Delta\bar{\nu}$ 1715 in lieu of $\Delta\bar{\nu}$ 1735, while the ketonic derivatives of cyclohexene and benzene yield $\Delta\bar{\nu}$ 1673 for the C=O as compared with $\Delta\bar{\nu}$ 1705 for the normal ketones. Thus conjugate C=C with C=O and this will reduce the characteristic carbonyl shift from 10 to 35 wave numbers and, as has been pointed out previously, the C=O will reduce the C=C shift by as much as 40 wave numbers.

One of the most peculiar cycloölefins investigated is cedrene, which presumably has the formula



This compound was investigated by Matsuno and Han (423). These authors found one hundred and nineteen Raman lines, of which $\Delta\bar{\nu}$ 1666 is attributed to the ethylenic linkage. A very careful analysis was made of the Raman lines observed and an attempt was made to correlate them with a possible structure. A frequency at $\Delta\bar{\nu}$ 1375 is associated with the structure  $\underset{\displaystyle CH_3}{—\overset{}{C}}=C—$. While the results are not conclusive, this is an excellent example of the method employed in the application of Raman spectra to the delineation of molecular constitution. Other examples will be given after the discussion of benzene and its derivatives.

L. The Raman spectra of aromatic hydrocarbons

1. Benzene. Benzene has been more extensively investigated than any other compound. It is impossible to cite in the text all the contributions of the large number of workers who have examined this compound and its derivatives. The material presented has been chosen with the view of presenting typical effects of substitution and the Raman spectra of some of these compounds, rather than a detailed summary of each compound.

The Raman spectrum of benzene has been determined carefully by Grassmann and Weiler (272). They observed forty-one lines whose frequency shifts and intensities are as follows: $\Delta\bar{\nu}$ 404 (1), 607 (8), 692 (1), 781 (0), 802 (0), 824 (½), 849 (4), 971 (1), 984 (2), 993 (15), 1005 (1), 1034 (1), 1176 (4), 1285 (0), 1326 (½), 1402 (2), 1449 (0), 1480 (0), 1584 (12), 1606 (8), 1697 (0), 1827 (½), 1936 (1), 1988 (½), 2030 (½), 2128 (½), 2296 (1), 2358 (½), 2455 (1), 2545 (1), 2618 (2), 2688 (½), 2927 (1), 2949 (4), 3049 (8), 3063 (12), 3166 (3), 3187 (4), 3463 (0), 3680 (0), 3916 (0). It is believed that these may be explained as a result of ten ground frequencies and their combinations. These fundamental frequencies are given in table 22. Two of these, indicated by *, are members of doublets. The frequencies most important are $\Delta\bar{\nu}$ 992, 1585, 1606, 3049, and 3063. The first of these is attributable to the carbon to carbon vibration, the second two to the C=C, and the last two to the linear carbon-hydrogen oscillation. The frequency at $\Delta\bar{\nu}$ 984 is attributed by Grassmann and Weiler and by Bhagavantam (54) to the influence of the carbon isotope of mass 13. Langseth (397) has previously explained the fine structure of $\Delta\bar{\nu}$ 455 in carbon tetrachloride as due to the isotopes of chlorine. Bhagavantam, who has investigated the fine structure of $\Delta\bar{\nu}$ 992 in benzene, 1188 in cyclopropane and 993 in ethane, comes to the conclusion that all these lines have satellites whose intensities and frequency displacements can be accounted for on the assumption that one of the carbon atoms has a mass 13. The shift $\Delta\bar{\nu}$ 992 is almost perfectly polarized, its depolarization constant being 0.05, and consequently represents an inactive oscillation which appears only weakly in infra-red absorption in view of its symmetrical vibration. This frequency appears in practically all the derivatives of benzene in a slightly shifted position and with variations in intensity, depending on the complexity of the substitution. Under high dispersion Howlett (319) has broken this line into five components. Bhagavantam (42) attributes $\Delta\bar{\nu}$ 607, 851, 992, 1181 to the hexagonal carbon ring in benzene, among which $\Delta\bar{\nu}$ 607 is attributed to the alternate expansion and contraction of the hexagon, and $\Delta\bar{\nu}$ 851, 1181 to the unsymmetrical modes of oscillation of the extension type. He has ascribed the doublet frequency $\Delta\bar{\nu}$ 1584 and 1606 to oscillations especially involving the hydrogen atom. This raises the question as to the Kekulé or the centric or the Claus formula for benzene. It is one of the anomalies in the elucidation of the structure of organic compounds,

TABLE 22

Fundamental frequencies of benzene

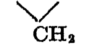
	$\Delta\bar{\nu}$	i		$\Delta\bar{\nu}$	i
ν_1	400	1	ν_7	1176	4
ν_2	606.8	8	ν_8	1480	0
ν_3	692	1	ν_9	1585.4	12
ν_4	849	4	ν_9*	1606.4	8
ν_5	992.5	15	ν_{10}	3049	8
ν_6	1034	1	ν_{10}*	3063.6	12

in general, that what would seem to be one of the simplest applications, namely, the differentiation of these two structures, has not met with conspicuous success. Neither has the application of the mechanical models of Andrews and his coworkers solved this problem. As pointed out in the beginning, it is possible that the rigid chemical method of depicting formulas is too static and not sufficiently dynamic. Heretofore, Raman spectra have preceded rather than followed the interpretation of bonds on the basis of resonating bonds as employed more recently by Pauling. The triple-bond structure of nitrous oxide and possibly that of carbon monoxide are pertinent examples. In the case of benzene it was originally presumed that shifts in the region of $\Delta\bar{\nu}$ 1585 and 1608 were due to the same type of double bond as found in the ethylenic linkage. Subsequently this was questioned. Wilson (647, 648), in his very competent analysis of the spectrum from a mathematical view, attributes $\Delta\bar{\nu}$ 1584 to an accidental degeneration. Originally Kettering, Shutts, and Andrews (331) assumed that the evidence was in favor of the double-bond structure from the vibration of the mechanical models. Murray, Deitz, and Andrews (465) conclude that there are no effective forces acting between the carbon atoms para to one another in the ring, and that this, therefore, is evidence against the centric formula, and that with the assumption that the average force constant of the carbon to carbon bond in the ring is roughly one and one-half times those of the normal homopolar single bonds, the results are in accord with the resonance formula of Pauling or the Kekulé formula. Bonino (69, 71) has discussed the entire situation in regard to benzene in considerable detail. He believes that the line at $\Delta\bar{\nu}$ 1580 is somewhat analogous to the line for C=C, and it is because of other conditions that there is doubt whether this represents a true double bond. Bonino and Manzoni-Ansidei (92) doubt the existence of ethylenic linkage in benzene. Truchet and Chapron (601) express the view that the shift at $\Delta\bar{\nu}$ 1584 or 1608 is well within the variation in the C=C shift observed in other compounds whose structure is generally accepted as containing a C=C group. Lespieau and Bourguel (405) and Bourguel (97) consider these shifts as arising from double bonded carbon. This shift may actually vary from $\Delta\bar{\nu}$ 1409 in thiophene to $\Delta\bar{\nu}$ 1679 in trimethylethylene, excluding $\Delta\bar{\nu}$ 1074 observed in allene. In any case it does not seem to be tenable that this shift can owe its origin to any carbon and hydrogen vibration, since it is present in pentachlorobenzene and slightly shifted in hexachlorobenzene.

It is believed by this writer that while the Kekulé notation may represent too static a picture, for the purposes of representation of the modification in the changes of Raman spectra as a function of constitution $\Delta\bar{\nu}$ 1580 or 1608 may be treated in the same fashion as any other C=C

TABLE 23

Fundamental frequencies of benzene and its monosubstitution derivatives

DERIVATIVES	$\Delta\bar{\nu}$						
C_6H_6	605(3)	992(10)		1178(3)		1605(1) 1584(3)	3057(1) 3060(5)
a. Hydrocarbon derivatives							
$C_6H_5CH_3$	622(2)	1002(8)	1029(1)	1154(1)	1209(3)	1604(2)	3054(5)
$C_6H_5CH_2CH_3$	620(2)	1003(8)	1029(1)	1157(3)	1203(2)	1604(5)	3052(5)
$C_6H_5CH{=}CH_2$	623(5)	999(7)	1029(1)	1154(1)	1205(8)	1601(10)	3057(8)
$C_6H_5C{\equiv}CH$	623(5)	1000(7)	1029(1)	1158(1)	1195(8)	1601(10)	3059(9)
$C_6H_5CH_2CH{=}CH_2$	623(5)	1000(7)	1029(1)	1158(1)	1205(5)	1599(10)	3057(8)
$C_6H_5CH{=}CHCH_3$	621(5)	999(8)	1031(1)	1149(5)	1210(8)	1599(10)	3055(8)
 $C_6H_5-CH-CH_2$, CH_2	623(5)	999(7)	1026(1)	1156(1)	1220(8)	1604(8)	3061(8)
$C_6H_5-CH_2-C{\equiv}CH$	623(1)	1000(8)	1033(1)	1158(1)	1200(5)	1601(7)	3059(8)
$C_6H_5C_6H_5$	611(1)	994(5)	1022(2)	1146(1)	1191(1)	1589(3) 1609(5)	3047(8)
$C_6H_5CH_2C_6H_5$	623(4)	1012(8)	1037(4)	1145(2)	1175(4)	1593(6)	3054(4)
$C_6H_5CH_2CH_2C_6H_5$	619(3)	1002(10)	1032(4)	1153(2)	1200(4)	1600(5)	3052(4)
$C_6H_5CH{=}CHC_6H_5$ (*trans*)	620(3)	1004(10)			1188(15)	1590(15)	
$C_6H_5CH{=}CHC_6H_5$ (*cis*)	615(2)	1000(10)	1027(2)	1150(4)	1190(4)	1596(10)	3059(4)
$C_6H_5C{\equiv}C_6H_5$	621(2)	997(15)	1028(1)	1140(15) 1155(2)	1174(2) 1188(2)	1590(20)	
b. Benzyl compounds							
$C_6H_5CH_2Cl$	619(4)	1000(3)	1034(1)	1159(1)	1211(1)	1600(1)	3054(3)
$C_6H_5CH_2NH_2$	622(4)	1001(8)	1028(2)	1156(4)	1201(4)	1606(4)	3055(8)
$C_6H_5CH_2OH$	610(0)	1000(3)			1196(1)	1594(2)	3050(3)
$C_6H_5CH_2NO_2$	623(4)	1005(8)	1029(3)	1160(2)	1197(3)	1596(5)	3059(4)
$C_6H_5CH_2CN$	620(2)	1007(4)	1030(1)		1187(2)	1597(2)	3057(4)

:. Various d· .vatives							
C_6H_5OH..	614(2)	1002(5)	1024(3)	1170(3		1598(3)	:059(5)
C_6H_5CHO. .	615(3)	1001(8)	1023(1)	1164(5)	203(6	1597(10	:063(5)
C_6H_5COCl...	615(3)	1003(6)	1028(2)	1168(2)	206(3	1592(6)	.067(4)
$C_6H_5COOCH_3$	613(3)	1000(7)	1023(1)	1160(1)		1602(10	3070(5)
$C_6H_5COCH_3$..	613(3)	999(5)	1025(3)	1155(1)		1597(6)	3063(4)
C_6H_5Cl.......	615(6)	1001(10)	1021(6)	1156(4)		1581(6)	30
C_6H_5Br......	608(1)	1000(4)	1022(2)	1159(1)		1576(2)	3060(5)
C_6H_5I........	610(3)	998(7)	1012(4)	1158(2)		1568(5)	3054(2)
$C_6H_5NH_2$.....	617(3)	996(10)	1029(5)	1147(3)		1601(10)	3046(4)
$C_6H_5NHC_6H_5$.	620(2)	1000(12)	1030(5)			.603(2	3064(3)
$C_6H_5NO_2$	604(1)	1000(3)				.587(4	3052(1)
C_6H_5CN.	619(1)	998(5)		1175(2)	)0(3	595(4	3063(4)

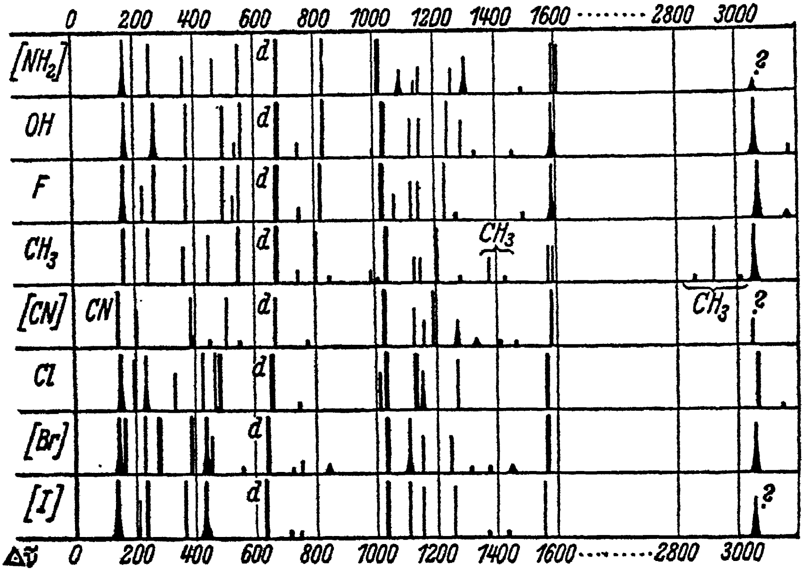


FIG. 17. The Raman spectra of ortho-substituted chlorobenzenes (after Kohlrausch and Pongratz)

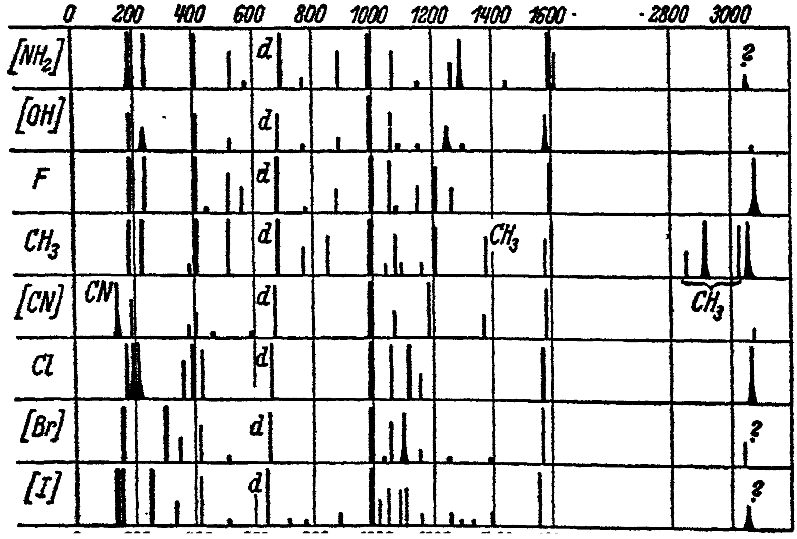


FIG. 18. The Raman spectra of meta-substituted chlorobenzenes (after Kohlrausch and Pongratz)

line. It is difficult to conceive that the method of treating cyclopentene, cyclohexene, or their respective dienes and the terpenes should be different from that for benzene and its derivatives. From the point of view of the analysis of their spectra, therefore, these compounds will be considered in the same fashion as any other hydrocarbons.

1. Monosubstituted benzenes. In an extensive series of publications Kohlrausch and Pongratz (355, 360, 361, 365, 366) and Dadieu, Pongratz, and Kohlrausch (191) have determined the effect of substitution on benzene. Murray and Andrews (462, 463) and many others (note bibliography) have also investigated monosubstituted and polysubstituted benzenes. In table 23 are given the principal lines from benzene and its monosubstitution derivatives. These data are taken from Bourguel (100) and are based partially upon observations of Dadieu, Pongratz, and Kohlrausch, and of Kohlrausch and Pongratz.

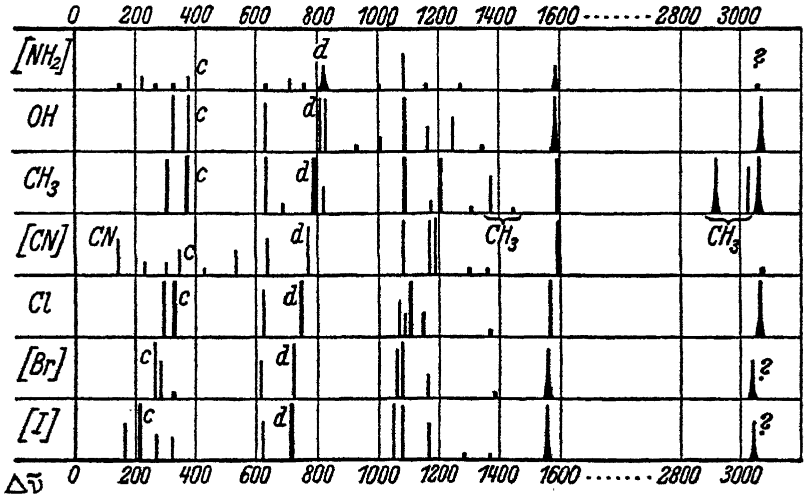


FIG. 19. The Raman spectra of para-substituted chlorobenzenes (after Kohlrausch and Pongratz)

2. Disubstituted benzenes. The effect of disubstitution in benzene is illustrated in figures 17, 18, and 19, which illustrate the behavior of substituted chlorobenzenes containing different substituent groups (367). Figure 17 represents the effect of ortho substitution, figure 18 meta substitution, and figure 19 para substitution. On considering first figure 19, it is quite evident that there are at least seven frequencies which remain reasonably constant throughout all the compounds of benzene and its monosubstitution products. These are frequencies which are dependent upon the structural features of either the ring or the ring double bond. In those cases where a double bond occurs external to the ring the shifts characteristic of the ring double bond alone are given. The C—H oscillation varies from approximately $\Delta\tilde{\nu}$ 3047 to 3070 depending on the nature of the substituent group. It is noticeable that there is a reinforcement of the intensity of the C=C shift when there is a double bond external to the ring. This shift remains constant within 15 wave numbers, irrespective of the nature of the hydrocarbon substituent group. If, however, the substituent group is not a hydrocarbon radical but some other derivative, there is a greater alteration in the C=C frequency. This is particularly notable in the case of the halogens, where there is a progressive decrease in the frequency with the increase in molecular weight of the halogen. There is likewise an effect on the C—H oscillation which decreases progressively from the $\Delta\tilde{\nu}$ 3066 to 3054 with the same halogen substitution. If, however, the halogen is removed from direct contact with the ring, as in benzyl chloride, the effect is much smaller. There is an appreciable reaction from conjugation with the carbonyl group. The net result, however, is that the effect of substitution on the ethylenic shift is less marked than in the case of the normal ethylenes, the cyclopentenes, or the cyclohexenes. In view of the conjugate nature of the ethylenic linkage in benzene it is of some importance that a substituent on one carbon atom in the aromatic nucleus must necessarily be attached to one ethylenic linkage and removed by one carbon from the next double bond. Nevertheless, this unsymmetrical arrangement results in only one strong Raman shift in this region. This would seem to give some weight to the dynamical conception of the nucleus in this case.

While it has been observed that the substitution of a methyl group in the aliphatic ethylenes and in cyclopentene and cyclohexene markedly increases the ethylenic shift, the passage from benzene to toluene causes only a very slight modification. Similarly in going from the methyl derivatives of unsaturateds, including cyclopentene, to the aldehyde derivative there is a marked decrease in the ethylenic shift. By progressing from toluene to benzaldehyde, however, the decrease is only about one-third of that observed in the other compounds. On the other hand, a similar progression of the carbonyl derivatives indicates that the esters of the aliphatic unsaturateds and of cyclopentene have the largest carbonyl shifts and the aldehydes the least. By comparing methyl benzoate with benzaldehyde one observes a change in $\Delta\tilde{\nu}$ from 1647 to 1689. This, therefore, is in the opposite direction from the frequency changes observed with the other compounds and is compatible with the classical effect of phenyl groups as contrasted with the alkyl radicals.

3. Polysubstituted benzenes. In the disubstituted aromatics there are definite progressive changes in the Raman spectra depending on the sub-

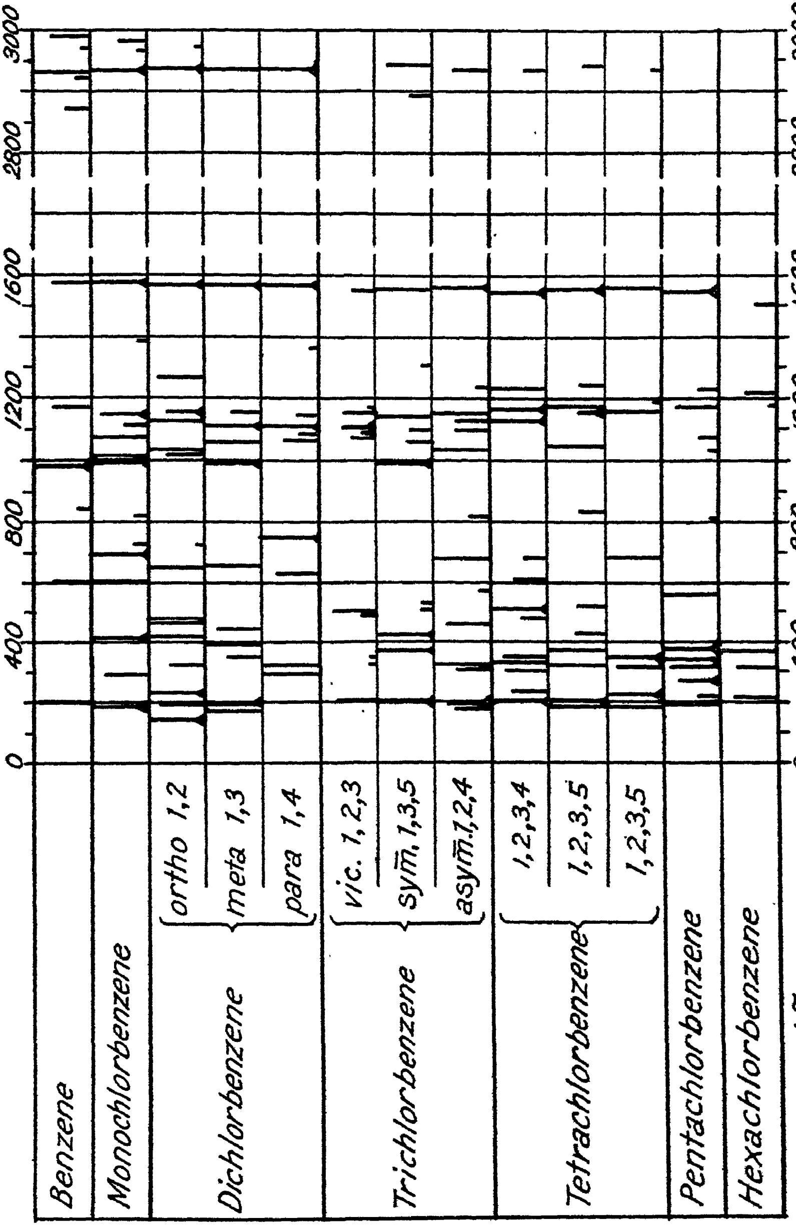


FIG. 20. The Raman spectra of polysubstituted chlorobenzenes (after Dadieu, Kohlrausch, and Pongratz.

stituent groups and the position of substitution. Kohlrausch and Pongratz have indicated some of these in the figures cited. It is particularly noticeable in the differences in para-substituted chlorobenzene as compared with the ortho and meta derivatives. In the substituted xylenes the frequency of the linear C—H shift increased from $\Delta\bar{\nu}$ 3047 in *o*-xylene to $\Delta\bar{\nu}$ 3070 in *o*-chlorotoluene. Kohlrausch and Pongratz (365) give the frequency of aliphatic C—H binding in the series from toluene to pentamethylbenzene as being $\Delta\bar{\nu}$ 1378 (6), 1445 (3), 2728 (1), 2862 (4), 2916 (8), 3019 (4). The effect of multiple substitution on the double-bond linkage is shown in table 24, taken from data of Kohlrausch (340). The shifts in the entire spectra as a result of multiple substitution are shown in figure 20, which gives the spectra of the polysubstituted chlorobenzenes (191).

TABLE 24

The change in C=C *shift as a function of substitution in polysubstituted benzene*

SUBSTANCE	POSITION OF SUBSTITUENT GROUPS	$\Delta\bar{\nu}$		
		X = Cl	X = CH_3	
C_6H_6			1584(3)	1606(1)
C_6H_5X	1	1580(7)	1580(1)	1603(5)
$C_6H_4X_2$	1, 2	1572(8)	1584(1)	1606(5)
	1, 3	1572(8)	1590(1)	1612(4)
	1, 4	1572(7)	1575(1)	1616(6)
$C_6H_3X_3$	1, 2, 4	1564(8)	1567(4)	1617(7)
	1, 3, 5	1563(6)		1604(6)
	1, 2, 3	1554(2)		
$C_6H_2X_4$	1, 2, 4, 5	1563(5)	1560(4)	1620(5)
	1, 2, 3, 5	1558(6)	1572(3)	1614(7)
	1, 2, 3, 4	1552(8)		
C_6HX_5	1, 2, 3, 4, 5	1553(5)	1572(3)	1607(4)
C_6X_6	1, 2, 3, 4, 5, 6	1503(2)		1565(1)

The changes in the spectra of benzene with progressive halogen substitution have been painstakingly investigated by Murray and Andrews (463). These authors observed new lines not observed by Dadieu, Kohlrausch, and Pongratz and have confirmed most of their observations. In particular they have found multiple lines in the $\Delta\bar{\nu}$ 1600 region, most of which were not previously observed and are rather weak. In all the halogen derivatives very strong frequencies are noted between $\Delta\bar{\nu}$ 200 and 400. The Raman spectrum of fluorobenzene resembles the spectra of the heavier monohalogen derivatives of benzene, but shows a certain marked difference. It is very similar to the spectrum of toluene, whose side chain has approximately the same mass as fluorine. Between $\Delta\bar{\nu}$ 1000 and 1200 the fluorobenzene spectrum is very different from the other halogen derivatives. This is indicated in figure 21, which shows the effect of different halogen substitution. The frequencies indicated between $\Delta\bar{\nu}$ 2200 and 2600 are stronger in the figure, in order to indicate them, than actually observed.

4. Summary. While the characteristic frequencies of the double and triple bonds and the influence of substitution on them have been given in detail in tables 7 to 13, 15, 19 to 21, 23, and 24, table 25 is included to give a rough summary of these conclusions.

In this table the shifts for the unsubstituted hydrocarbon are given in parentheses. In column 1 is the type of linkage whose shifts as a function of chemical constitution are given in columns 3 to 8 inclusive. When this linkage is conjugated with another of the same or different types this is indicated in column 2. When the conjugate double bond is in the phenyl radical this is indicated. When two shifts are paired, it indicates a possibility of a marked difference usually attributed to *cis-trans* isomerism. It is to be borne in mind that these shifts are not constant values, but will vary in each homologous series depending on the position and character of substituent groups.

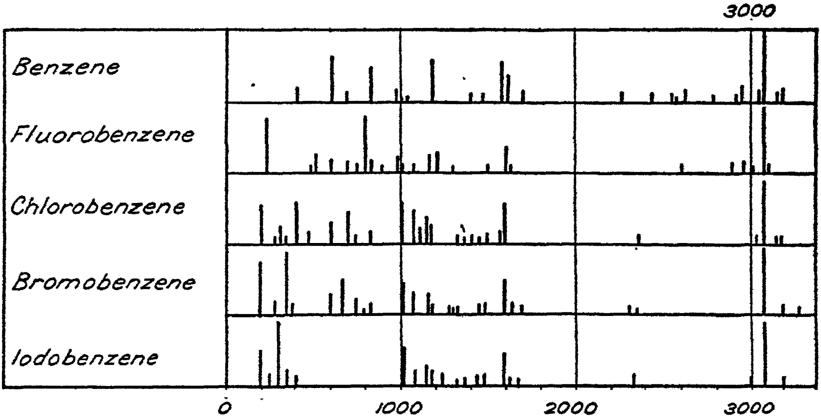


FIG. 21. The Raman spectra of halogen substituted benzenes (after Andrews)

It has been demonstrated in general that each type of chemical linkage so far discussed has its characteristic frequencies, and each kind of molecule gives rise to a series of Raman shifts whose frequencies and intensities depend upon the molecular configuration. It is thus often possible to determine the constitution of some compounds and the composition of certain mixtures.

Lespieau and Bourguel (404), for example, determined the Raman spec-

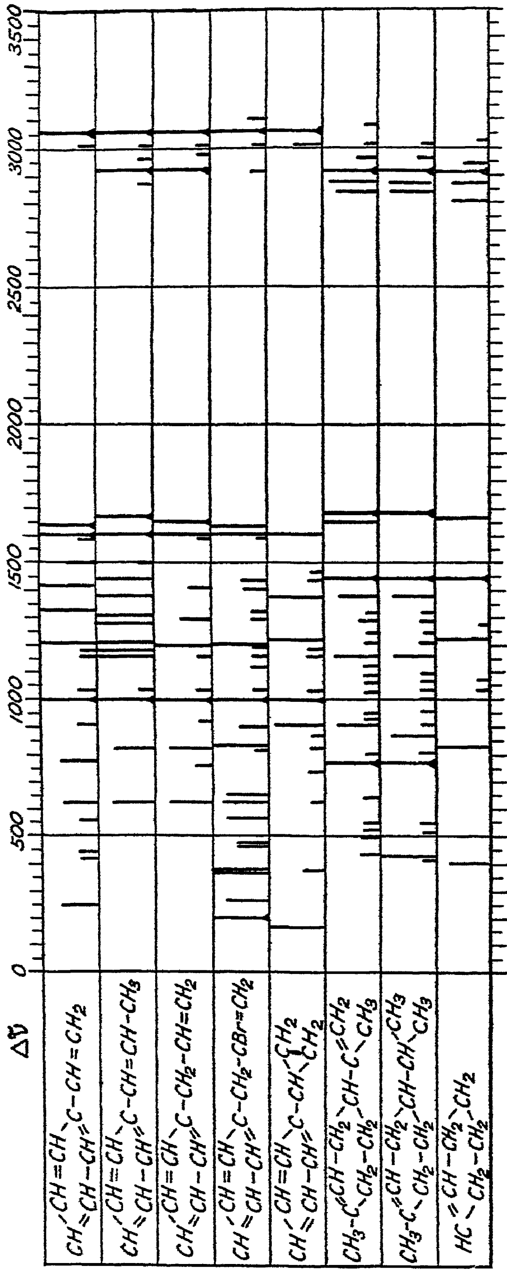


FIG. 22. The Raman spectra of some derivatives of benzene and cyclic compounds containing internal and external double bonds (after Lespieau and Bourguel)

TABLE 25

Influence of substitution on C=C, C=O, *and* C≡C *linkages*

	$\Delta\bar{\nu}$					
Linkage	Hydrocarbon	Aldehyde	Ketone	Acid	Ester	Anhydride
			Aliphatic hydrocarbons			
1 2						
*C=C	(1620)1644–1678					
C=C, C=C	1634–1660					
C=C, C=O		1620–1647	1600	1638	1664–1679	
		1720	1705	1654	1735	
C=O, C=O			1725	1735	1735	1750, 1820
C=O, C=C		1689	1668		1740	
			Cyclic compounds			
		C_5				
C=C	(1615)1658					
C=C, C=C	1500					
C=C, C=O		1616			1631	
C=O			1735			
C=O, C=C		1676			1715	
		C_6				
C=C	(1650)1675					
C=C, C=C	1576 1615–1635					
C=C, C=O			1638		1672	
C=O			1712		1740	
C=O, C=C			1670		1735	
C=C (cf. benzene)	(1584) (1605)1604	1597	1597	1601	1602	
C=O, C=C(phenyl)		1690	1677	1670	1724	
		C_7				
C=C	(1651)1672					
		C_8				
C=C	(1604)					
			Acetylenes			
C≡C	(2119), 2236, 2293				2238	
C≡C, C=C(phenyl)	2221, 2241					
C=C(phenyl), C≡C	1600					
C≡C, C≡C	2250, 2304					
C=O, C≡C					1715	

* The $\Delta\bar{\nu}$ are given for the linkage indicated in column 1.

tra of three isomers, namely, isoallylbenzene, benzylethylene, and a bicyclic compound which was believed to be phenylcyclopropane. The ease with which the last compound will break down its bicyclic structure made it difficult to determine by chemical means its molecular constitution. The following Raman spectra, however, were observed for isoallylbenzene: $\Delta\bar{\nu}$ 2599 (10), 1645 (1), 1663 (10). The highest of these shifts is fairly characteristic of a disubstituted ethylenic linkage, and the lowest is characteristic of the ethylenic linkage in the phenyl radical. For benzylethylene were observed $\Delta\bar{\nu}$ 1599 (8) and $\Delta\bar{\nu}$ 1645 (8), where $\Delta\bar{\nu}$ 1645 is the shift for a monosubstituted ethylene and the 1599 shift has the same significance that it has in isoallylbenzene. For the supposed bicyclic compounds was observed $\Delta\bar{\nu}$ 1604 (8), which demonstrates that no unsaturated side chain was present. Furthermore, the C—H shifts in isoallylbenzene were $\Delta\bar{\nu}$ 2864 (2), 2920 (8), 2968 (2), and 3055 (8). In benzylethylene were found $\Delta\bar{\nu}$ 2914 (8), 2978 (10), and 3057 (8). In the other compound, however, were observed only $\Delta\bar{\nu}$ 3007 (6) and 3062 (6). The lack of frequencies below $\Delta\bar{\nu}$ 3000 indicates conclusively the absence of side chains containing a methyl group. The shift $\Delta\bar{\nu}$ 3062 belongs to the hydrogen attached to the benzene ring and $\Delta\bar{\nu}$ 3007 is characteristic of the hydrogen attached to a cyclopropane nucleus which appears at $\Delta\bar{\nu}$ 3011 in cyclopropane and $\Delta\bar{\nu}$ 3015 in methylcyclopropane. The complete Raman spectra of these compounds and of limonene, carvomenthene, and cyclohexene are given in figure 22 to indicate the interrelations between external and internal double bonds.

M. The Raman spectra of the terpenes, terpene derivatives, and terpenoids

Perhaps one of the most fruitful applications of the Raman effect lies in the field of the terpenes. Many of their structures are as yet questioned, and the mixtures found in practice may be extraordinarily complex.

It may be noted in figure 22, in comparing the spectra of the last three compounds and their constitutional formulas, that there are very strong similarities. Limonene has an external double bond of the general formula $R_1R_2C{=}CH_2$, whose frequency shift is in the neighborhood of $\Delta\bar{\nu}$ 1650. Its internal double-bond shift $\Delta\bar{\nu}$ 1681 is similar to that of methylcyclohexene, $\Delta\bar{\nu}$ 1675. Carvomenthene likewise gives $\Delta\bar{\nu}$ 1681. Consequently the magnitudes of the frequency displacement in these compounds are compatible with their presumed structure.

Nevgi and Jatkar (473) have studied a series of terpenes to determine if there were any differences in the frequency shifts from terpenes identical except for optical activity. These results are indicated in figure 23.

The abbreviated formulas for these compounds are given in the figure. All these terpenes contain double bonds; some of these double bonds, however, are within the ring and some without, and their position is not always identical. The Δ^3-carene and Δ^4-carene are identical except for the position of the double bond in the cyclohexene ring and its relation to the

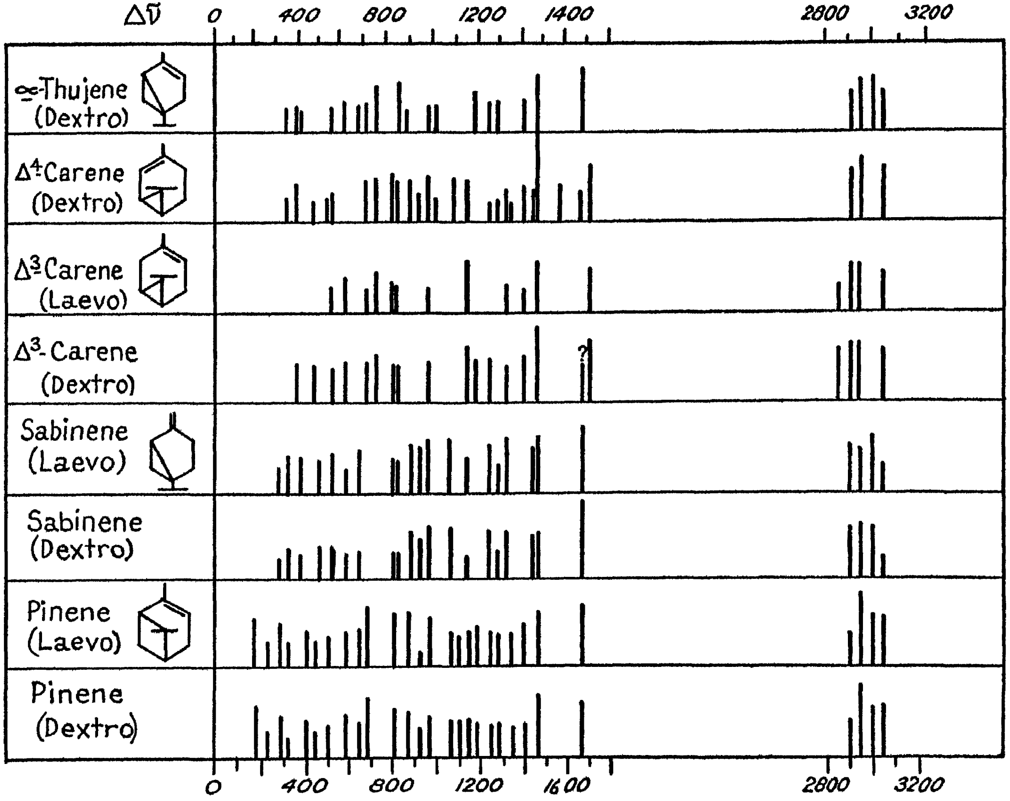


FIG. 23. The R pe me pol yc after Nevgi and Ja

C_3 ring. The spectra so far as the C═C shift is concerned are somewhat different, *d*-Δ^4-carene giving $\Delta\bar{\nu}$ 1554, 1639, and 1670, as compared with $\Delta\bar{\nu}$ 1641 and 1683 for *d*-Δ^3-carene. The *l*-Δ^3-carene has $\Delta\bar{\nu}$ 1685, the only observed frequency shift in the region which is comparable with that from substituted cyclohexene. The other isomers containing a ring double bond give, however, a lower frequency shift, such as $\Delta\bar{\nu}$ 1642 for *d*-α-thujene and $\Delta\bar{\nu}$ 1657 for the *d*- and *l*-α-pinenes. Apparently when the bridge in the cyclohexene nucleus is so situated that it is close to the ring double bond as in Δ^4-carene and the pinenes, the C═C frequency is reduced. If, however, it is more distantly removed as in Δ^3-carene, the normal cyclohexene shift is present. The two sabinenes give identical C═C shifts at $\Delta\bar{\nu}$ 1653, which is an approximately correct position for a compound of the type $R_1R_2C{=}CH_2$.

All these compounds show a shift near $\Delta\bar{\nu}$ 1440 characteristic of the CH_2 group. The pinenes, however, possibly show a rotational spectrum of the hydrogen around the carbon. The linear C—H oscillation occurs at $\Delta\bar{\nu}$ 3008 in the carenes and in the thujenes, at $\Delta\bar{\nu}$ 3030 in the pinenes, and at $\Delta\bar{\nu}$ 3046 in the sabinenes. While these shifts are given an intensity of 1 to 3 in these terpenes, it is to be noted that they are apparently absent or very much weakened in ordinary cyclohexene derivatives. The conclusion is that while these isomers differ one from another, particularly in the lower frequency region, and they may thus be distinguished without too much difficulty, there is no apparent difference in the intensity or magnitude between the dextro and levo forms of the same compound.

Hayashi (302) has discussed the alkyl derivatives of cyclohexane and cyclohexene with particular reference to their Raman spectra in connection with the terpene derivatives. He observes that the methyl-, ethyl-, and isopropylidenecyclohexanes have $\Delta\bar{\nu}$ 1655, 1676, and 1674, respectively, and the substituted cyclohexenes have shifts close to that expected from multisubstituted ethylenes (299, 300).

Bonino and Cella (82, 86) have made a comprehensive investigation of the Raman effect of the terpenes and their derivatives. In figure 24 are given the Raman spectra of a number of compounds which are not terpenes but are isomeric with them. These are geranial, geraniol, citronellol, citronellal, and linalool. These give for the corresponding C═C and C═O shifts respectively: geranial $\Delta\bar{\nu}$ 1640, 1681; geraniol $\Delta\bar{\nu}$ 1675; citronellol $\Delta\bar{\nu}$ 1675; citronellal $\Delta\bar{\nu}$ 1675, 1719; linalool $\Delta\bar{\nu}$ 1672 with 1646 very weak. In every case the double-bond shift falls within the expected frequency region for a compound of that composition. The Raman spectra of a number of terpenes as determined by Bonino and Cella (86) are given in figure 25, which shows the influence of molecular constitution on the respective shifts.

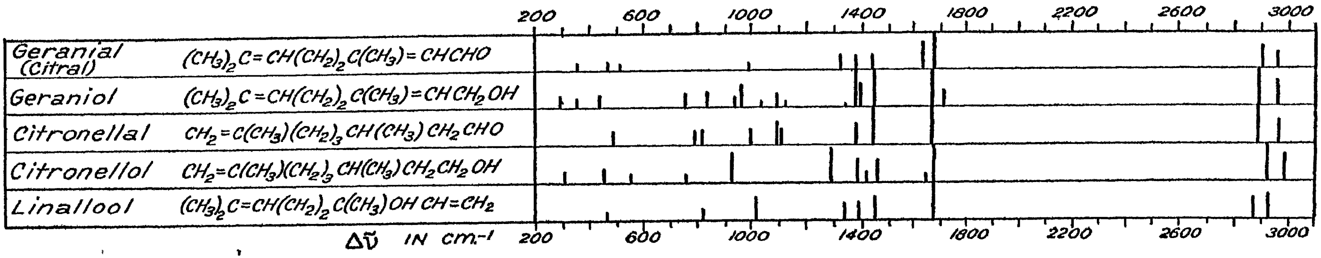


FIG. 24. The Raman spectra of some unsaturated aliphatic compounds isomeric with terpenes (after Bonino and Cella)

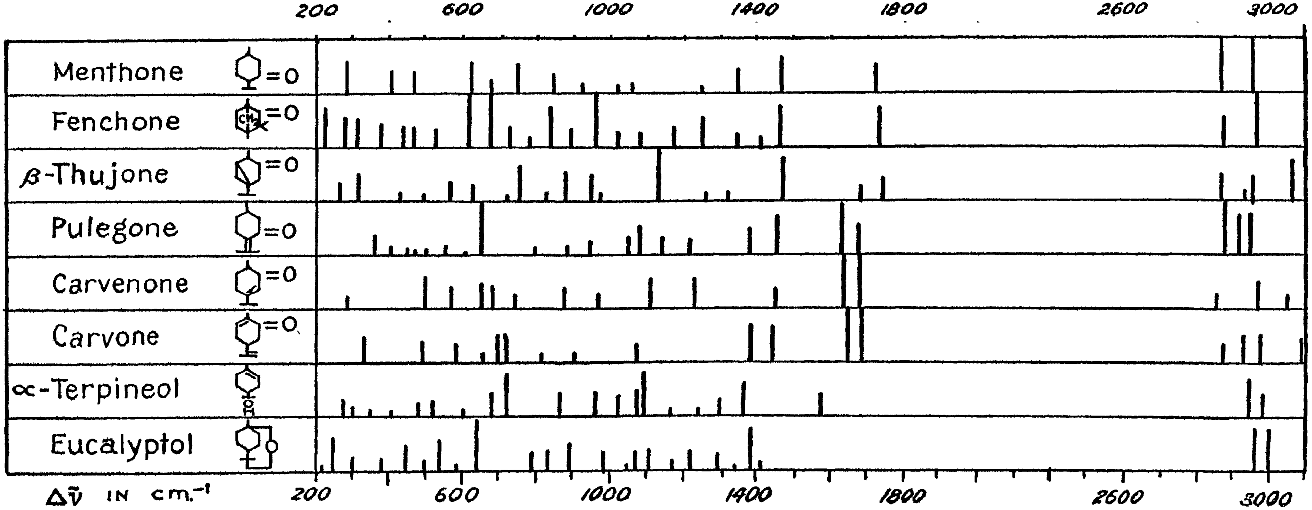
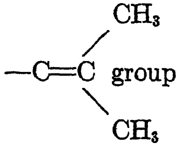


FIG. 25. The Raman spectra of some terpene derivatives (after Bonino and Cella)

On considering first the C—H shifts of these and other terpene compounds it is noticed that pulegone contains a  $-C=C\begin{array}{l}\diagup CH_3\\ \diagdown CH_3\end{array}$ group but no $>C=CH_2$ group. The maximum frequency for the C—H line obtained is, therefore, $\Delta\bar{\nu}$ 2951, which is in agreement with the precepts already enunciated. Carvenone possesses a ring —C=C— group which may give rise to $\Delta\bar{\nu}$ 3048 (1) for $C\leftrightarrow H$ (a type of shift which has not yet been observed in the substituted cycloölefins). This may also be present as $\Delta\bar{\nu}$ 3034 (3) in *d*-pinene and as $\Delta\nu$ 3082 (2) in limonene. Carvone having a $>C=CH_2$ group yields $\Delta\bar{\nu}$ 3085 (3). From the behavior of pulegone, menthone, and fenchone it is clear the C=O cannot be responsible for any C—H frequency in excess of $\Delta\bar{\nu}$ 3000, nor does a C_3 ring structure as in sabinane ($\Delta\bar{\nu}$ 2964) or the C_4 ring in pinane ($\Delta\bar{\nu}$ 2924) produce a frequency greater than $\Delta\bar{\nu}$ 3000. Sabinene, however, having both C_3 rings and $-C=CH_2$, shows $\Delta\bar{\nu}$ 3043 (3) and 3076 (3). β-Thujone, possessing no —C=C— and only a C_3 ring in addition to the C=O group, gives rise to $\Delta\bar{\nu}$ 3067 (4), according to Bonino and Cella (86). By employing tables 10, 11, and 25 and the known shifts for the alkylcyclohexanones and cyclohexenes, it is now possible to analyze the spectra of these terpenes with particular reference to the C=C and C=O shifts, and consequently determine if the observations are in accord with their constitution. This is shown in table 26.

It is evident that there is a general agreement between the observed and expected frequencies. In determining the calculated frequencies the effects of conjugation or multiple double bonds and the type of substitution are included. In pulegone, for example, the C=C and C=O shifts were corrected for conjugation, and in carvone the two frequencies $\Delta\bar{\nu}$ 1638 and 1670 were also corrected. However, the extranuclear double bond under the influence of multiple bonding should yield $\Delta\bar{\nu}$ 1600 to 1610, which is not present. When it is remembered that this double bond is removed from the C=O by a distance of two carbon atoms, it is not unreasonable, in the light of the evidence so far presented, to assume that the effect of conjugation is negligible and consequently the external C=C should yield a normal shift corresponding to $R_1R_2C=CH_2$ ($\Delta\bar{\nu}$ 1650). This is within the accuracy of these measurements and not distinguishable from the observed $\Delta\bar{\nu}$ 1646. The same conditions were employed in calculating the shifts for the compounds given in figure 24. If one double bond were far removed from any other in the molecule, it was considered to function as a separate unit and consequently yielded a shift the same as any other substituted ethylenic bond. If it were close to a C═O group the conjugation was considered effective. In citronellal conjugation was ignored. Geranial should yield $\Delta\bar{\nu}$ 1640 (conjugate C═C) and $\Delta\bar{\nu}$ 1689 (conjugate C═O) and a shift of conjugate type $R_1R_2C{=}CHR_3$ ($\Delta\bar{\nu}$ 1678). The latter shift, however, falls so close to the observed frequency at $\Delta\bar{\nu}$ 1681 that its presence is indeterminate. In geraniol and linalool the conjugation is ignored for the reasons already given.

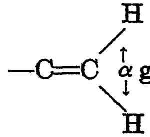
TABLE 26

The observed and calculated C═C *and* C═O *shifts for some terpenes*

COMPOUND	$\Delta\bar{\nu}$			
	Observed		Calculated	
	C═C	C═O	C═C	C═O
Pulegone	1617	1673	1600	1670
Carvenone	1632	1673	1638	1670
β-Thujone		1688 (2) 1750 (3)		1712
Menthone		1714		1712
Fenchone		1731		1712
Terpineol	1675		1675	
Carvone	1646	1673	1638	1670
α-Pinene	1656		1675	
l-Limonene	1658		1650	
	1680		1675	
Sabinene	1650		1650	
Menthene	1673		1675	
Geranial	1647	1681	1640	1689
			1678	
Citronellal	1675	1719	1650	1720
Citronellol	1675		1650	
Linalool	1672		1678	
	1646		1640	
Geraniol	1675		1678	

The net result of this is that, with the exception of β-thujone, perhaps α-pinene, and the C═C shift for citronellal and citronellol, the calculated results are in accord with the experimental observations. In view of the relative accuracy of measurements which are only accurate to within perhaps ± 5 wave numbers in comparison with other observers, this is a reasonably close agreement.

Citronellal and citronellol are generally considered as compounds of the type $R_1R_2C{=}CH_2$, so far as the first ethylenic shift is concerned. If, however, this were of the type $RCH{=}CHR_1$ (*trans*), the observed and calculated results would be practically identical. In view of the indeterminate nature of the structure of this compound from an organic chemical point of view, there remains a possibility that this may be the explanation. On the other hand, α-pinene and fenchone have an internal bridge structure which joins close to the double bond, and this may have some effect on the characteristic ethylenic shifts and might account for the departure in this case. It has already been remarked that β-thujone, as reported by Bonino and Cella, has an anomalous C—H shift ($\Delta\bar{\nu}$ 3067 (4)) indicative of a C=C group which is presumably not present. The observed shifts $\Delta\bar{\nu}$ 1688 (2) and 1750 (3) cannot be reconciled with the calculated frequencies. If there were an impurity present containing an unsaturated ethylenic linkage, however, this might explain the $\Delta\bar{\nu}$ 1688 and 3067 shifts observed.

These conclusions are not in agreement with Bonino and Cella, who discuss a reversed C=C frequency for carvenone, carvone, pulegone, and geranial. The lower frequencies near $\Delta\bar{\nu}$ 1650 are ascribed to C=O instead of C=C, and the larger frequency shift ($\Delta\bar{\nu}$ 1675) to C=C instead of C=O. This does not seem as logical or as compatible with the observation on the terpenes and other compounds as the explanation which is given. These authors have calculated the H—H angle in the  $-C{=}C\begin{smallmatrix}H\\ \updownarrow\alpha\\ H\end{smallmatrix}$ groups in these compounds as ranging from 104° in sabinane to 141° in carvenone. The force and deformation constants for the C—H linkage and the characteristic low frequency shifts in the terpene derivatives were determined. Any of the frequencies between $\Delta\bar{\nu}$ 1045 and 1450 have been accounted for on the basis of combination or rotational frequencies.

The differences in the Raman spectra of simple monocyclic terpenes possessing internal and external double bonds, and terpenes without double bonds are indicated in figure 26, taken from the data of Dupont, Daure, Allard, and Levy (216). These and other terpenes have been investigated by Daure (198, 199), Dulou (208), Dupont, Daure, and Allard (212), Dupont, Daure, Allard, and Levy (213, 214, 215), Dupont, Daure and Levy (217), Dupont and Gachard (218), Dupont and Joffre (219), Dupont, Levy, and Marot (220), Dupont and Dulou (211), Tabuteau (585), and Venkateswaran and Bhagavantam (628). Terpene mixtures have been analyzed by Dupont, Daure, Allard, and Levy (216). Bonichon (66, 67), after investigating a large number of alcohol and ester derivatives of the terpenes, concluded that there are enough distinguishing lines to differentiate the esters of a given terpene from each other and to determine the

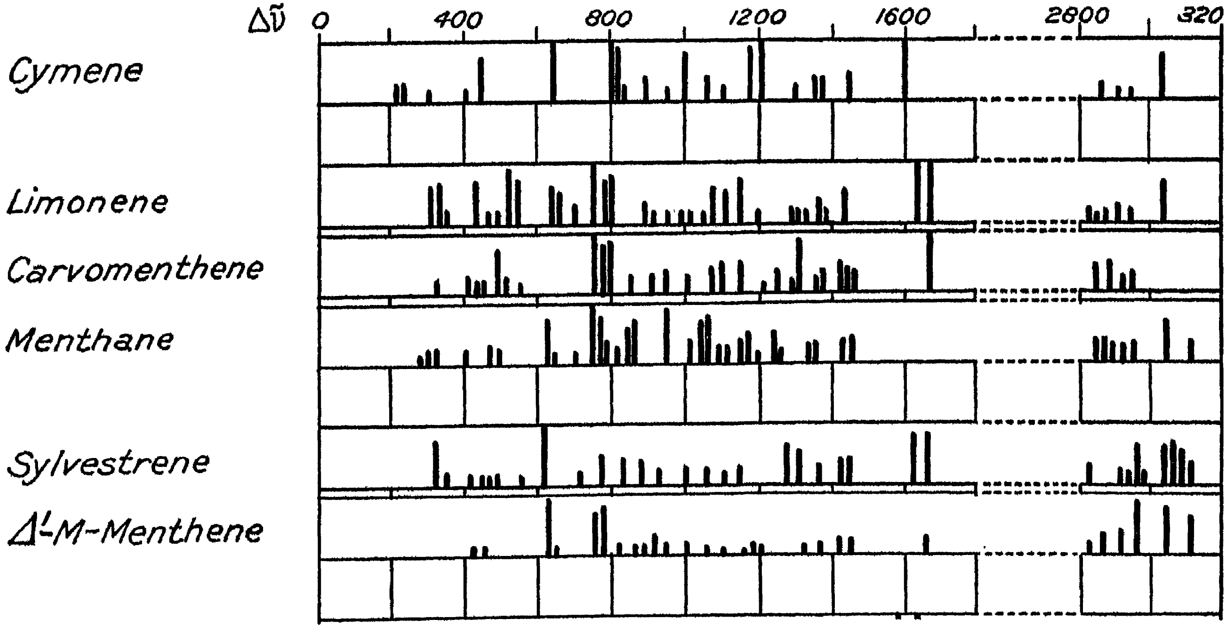
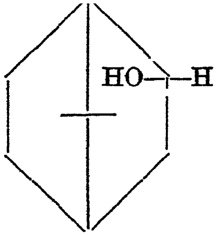
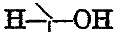


FIG The Raman spectra of some simple terpenes (after Dupont, Daure, Allard, and Levy) composition of mixtures of such closely allied compounds as the spacial isomers borneol and isoborneol. Borneol shows the characteristic frequencies $\Delta\bar{\nu}$ 600, 1230, 1300, and isoborneol $\Delta\bar{\nu}$ 627, 857, and 1023. The structures of these two compounds are indicated as follows:

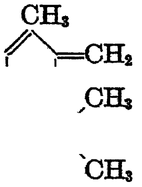


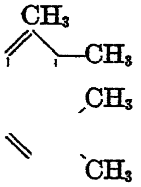
Borneol



Isoborneol

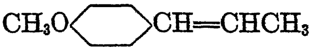
The analysis of the essence of terpenes, *Pinus longifolia*, by Raman spectra leads to the conclusion that there are present two forms of carene, namely, Δ^3-carene and β-carene (219). The distillation of oil of indienne likewise has been followed and shows the presence of pinene, β-pinene, and Δ^3-carene in successive distillates. Pinane and nopinane give identical Raman frequencies. Camphene yields $\Delta\bar{\nu}$ 1672 for the double bond, which is practically identical with that observed from β-pinene. There are, however, other lines which enable this compound to be distinguished from the pinenes. Tabuteau (585) has fractionated the essence of citronel of Java, and has found pinene, β-pinene, and limonene and other terpenes in the distillate. Dupont and Gachard (218) have investigated a number of the camphenes and other terpenes and the composition of complex mixtures. In particular a change in constitution on hydrogenation has been shown. This combination chemical and Raman-spectra method has also been followed by Dupont, Levy, and Marot (220), who studied the dehydration products of the terpinenes and terpineol. The action of heat on some terpenes has been investigated by Dupont and Dulou (211). The pyrolysis produced a mixture of terpenes of a new type, given the name pyronenes. These show $\Delta\bar{\nu}$ 1596 and 1657 for the double-bond linkage and to them are attributed the formulas:



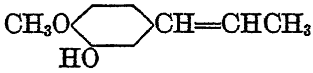


A detailed consideration of the terpenes could be continued indefinitely. This field of investigation is still somewhat in its infancy. It has been given this much space since the problems presented are of the same type as would be met in any complicated investigation. It is believed that the Raman spectra method has already made a genuine contribution in the delineation of the structure of the terpenes and in the identification of their constituents.

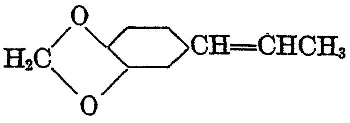
Before leaving entirely the question of the determination of the constitutional arrangements by means of Raman spectra based on the internal and external ethylenic linkages in benzene and its derivatives, there may be cited some work of Hayashi (299, 301). He determined the spectra of the following compounds:



Anethole[4]



Isoeugenol



Isosafrole

The principal frequencies obtained for anethole are $\Delta\bar{\nu}$ 1591 (9), 1644 (10); for isosafrole $\Delta\bar{\nu}$ 1601 (6), 1641 (7); for isoeugenol $\Delta\bar{\nu}$ 1604 (6), 1646 (7). The question here is whether there may exist geometric isomers of these compounds as found in nature. The frequency of the ethylenic linkage external to the ring is approximately 10 wave numbers lower than that observed for the *cis*-form of compounds of the type $R_1CH{=}CHR_2$ ($\Delta\bar{\nu}$ 1658). Therefore, it was originally concluded that the *cis*-form of these compounds probably predominated, because the *trans*-form of the ordinary disubstituted ethylenic linkage yields $\Delta\bar{\nu}$ 1673 (see table 9). On closer inspection, however, it was observed that the ether and hydroxy groups even in the para-position were not without their effect on the external ethylenic linkage. On comparing *trans*-isoallylbenzene $\Delta\bar{\nu}$ 1663, styrene $\Delta\bar{\nu}$ 1636, and *p*-methoxystyrene $\Delta\bar{\nu}$ 1620, there is shown a progressive decrease in the external ethylenic linkage. The constitution of isosafrole, isoeugenol, and anethole, so far as the side chain is concerned, is more like isoallylbenzene. One would expect, therefore, a shift near $\Delta\bar{\nu}$ 1663, but, as just shown, the influence of the methoxyl group is to lower the side chain frequency by approximately 15 wave numbers. This would diminish the expected $\Delta\bar{\nu}$ 1663 to $\Delta\bar{\nu}$ 1648, which is approximately the observed frequency. It is concluded, therefore, that these compounds exist ordinarily in the *trans*-form rather than the *cis*. It may be remarked that the influence of the methoxy group in the para-position is also noticeable by contrasting $\Delta\bar{\nu}$ 1700 for the C═O frequency in benzaldehyde with $\Delta\bar{\nu}$ 1687 observed in anisaldehyde. The conclusions, therefore, are compatible with the evidence. While this seems a perfectly straightforward deduction, it is somewhat in conflict in principle with the tenets which have been given in regard to the lack of influence of one group upon another if it were removed by any distance in the molecule.

N. The Raman spectra of diphenyl and its derivatives

Diphenyl and its derivatives have been investigated principally by Bonino and Manzoni-Ansidei (89). These are considered more as an entity rather than with the benzene derivatives and the terpenes, because they are thus considered in organic chemistry. Diphenyl, of course, is simply a phenyl derivative of benzene from the standpoint of Raman spectra. The observed spectra are very close to the spectra of benzene and its derivatives and have not been discussed in detail. It can only be remarked that the C—H shift occurs at approximately $\Delta\bar{\nu}$ 3067 and the C═C shift at $\Delta\bar{\nu}$ 1597. It is to be expected that substitution of the methyl groups in the diphenyl ring produces increasing complexity of the Raman spectra as a function of the number of substitutions. Dadieu and Kohlrausch (163) and Wood (658, 659) have investigated diphenyl. The hydrocarbon and halogen derivatives are confined to the observations of Bonino and Manzoni-Ansidei (89). It is to be admitted that this is a somewhat cursory dismissal of the subject, but from the characteristic linkage point of view there is little to be added.

O. The Raman spectra of polycyclic compounds

The Raman spectra of the polycyclic compounds are very much an extrapolation of the observations on benzene and cyclohexane and their derivatives. While naphthalene has been investigated by a great many observers, its derivatives have been investigated primarily by Bonino (69), Bonino and Cella (81, 85), Gockel (258), Hayashi (299), Mukerji (457, 458), and Ziemecki (671). Mukerji has studied dekalin, which is the completely saturated naphthalene, and tetralin, which represents the saturation of one of the benzene rings but not the other. These spectra have been compared to those of naphthalene and cyclohexane. Bonino and Cella have likewise observed the spectra of these compounds. There is a marked similarity among the entire group with the exception of the $\Delta\bar{\nu}$ 3046, which exists in naphthalene and tetralin but not in dekalin. In tetralin there is also $\Delta\bar{\nu}$ 2940. $\Delta\bar{\nu}$ 1037 appears weakly in dekalin and naphthalene and strongly in cyclohexane. $\Delta\bar{\nu}$ 699 in these observations corresponds to $\Delta\bar{\nu}$ 695 in cyclohexane. Many of the other shifts have the same significance which has been previously mentioned. For example,

$\Delta\bar{\nu}$ 1448 corresponds to the transverse oscillation of the hydrogen. $\Delta\bar{\nu}$ 1602, according to Bonino and Cella (81), occurs primarily in the tetralin compound; $\Delta\bar{\nu}$ 1583 in tetralin is absent in dekalin and is present as $\Delta\bar{\nu}$ 1573 in naphthalene. There are other differences in these compounds in the very low frequency shifts. Naphthalene shows $\Delta\bar{\nu}$ 3046 (1) and $\Delta\bar{\nu}$ 1573

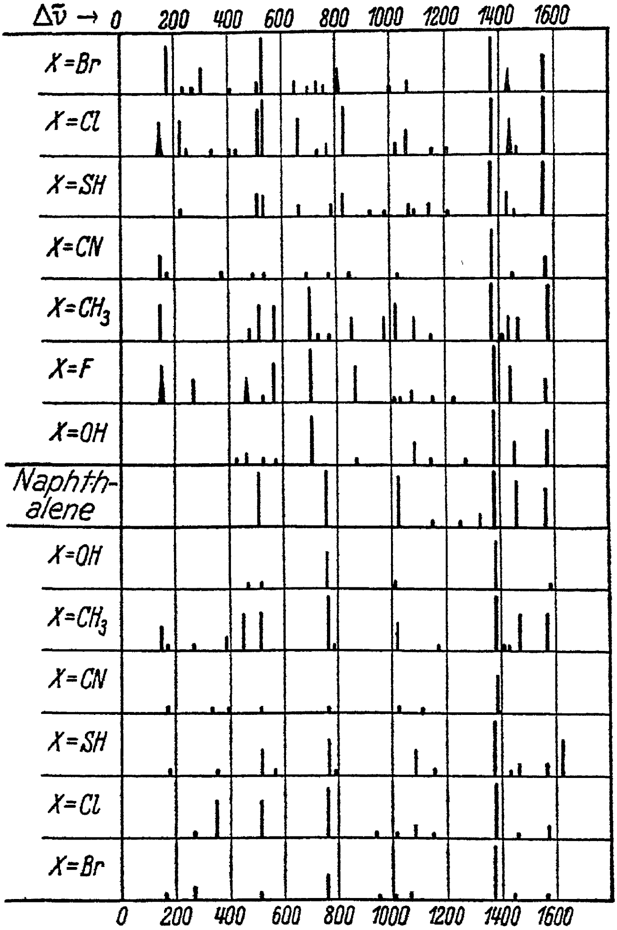


FIG. 27. The partial Raman spectra of naphthalene and its derivatives (after Gockel)

(3) for the C—H and C═C linkages. This is slightly lower than the C═C linkage in benzene. In α-bromonaphthalene this is reduced still further and becomes approximately $\Delta\bar{\nu}$ 1550 (5). The most complete survey of the naphthalene derivatives has been made by Gockel (258). This author studied the derivatives in the α- and β- (or 1,2-) positions. There is some

modification in the spectra depending upon the ring position of the introduced radical. There is a very profound modification in the spectra of naphthalene on substitution. Many of the lines, however, such as $\Delta\bar{\nu}$ 515, 1012, 1146, 1385, and 1573, remain fairly constant. The influence of substitution of different groups is shown in figure 27, which gives the middle and low Raman spectra of the naphthalene derivatives as a function of substitution. The upper half of the figure represents the substitution in the α-position and the lower half in the β-position.

Kohlrausch (343) has discussed the formula of naphthalene as a constitutional problem. Gross and Vuks (286, 287) have examined the very low frequency shifts of naphthalene. Some of these occur as low as $\Delta\bar{\nu}$ 45, 73, and 109, and are accompanied by wings, which are not connected with rotation as originally supposed, but with a slow oscillation characteristic of the crystal lattice.

P. The Raman spectra of organic sulfur compounds

Quasi-organic sulfur compounds such as carbon disulfide and the inorganic thiocyanates have been discussed by Hibben (311). The organic thioethers and mercaptans have been investigated by Bonino, Manzoni-Ansidei (90), Crigler (140), Dadieu, Pongratz, and Kohlrausch (186, 189), Kohlrausch and Köppl (346), Kohlrausch and Pongratz (366), Matossi and Aderhold (419), Meyer (437), Gopala Pai (268), Thatte and Ganesan (591, 593), and Venkateswaran (620, 623, 625).

The experimental observations by different workers are not in as close agreement as in other compounds. Nevertheless, it is quite apparent that the chain and C—H vibrations of the organic molecule are not seriously altered by the introduction of a sulfur atom. On the introduction of sulfur, however, new lines appear which are generally strong. This is the usual result when any heavy atom is introduced. There occur two inner vibrations, one characteristic of the C↔S linkage and one of the S↔H linkage. The latter appears near $\Delta\bar{\nu}$ 2570, which is unique for a shift in this region, and hence this linkage is easily identified. The increased mass as represented by the sulfur would tend to reduce the S↔H frequency in comparison to the C↔H one. The reduction would be greater as calculated than is actually observed, consequently there must be a comparative increase in the force constant of the S—H binding. The strongest C↔S shift falls near $\Delta\bar{\nu}$ 645, although this depends somewhat on the amount of branching, where the force constant is slightly low after correcting for the mass influence. In figure 28 are given the comparison spectra of the mercaptans, taken from the summary of Kohlrausch (339) and based on the work of various observers.

Venkateswaran (620) has indicated that the C—S shift in methyl mercaptan [Δν̄ 704 (10)] decreases to Δν̄ 659 (10) in ethyl mercaptan and to approximately Δν̄ 652 in the higher homologs. In the branched chain compounds this shift becomes first a doublet, and subsequently the lower frequency component of the doublet decreases in the magnitude of its shift with increased branching. The shift at Δν̄ 700 to 770, which persists in weakened form, is also characteristic of this linkage.

The thioethers contribute to the knowledge of the C—S shift. The stronger and more significant shifts of some of the thioethers are given in table 27, based on the results of Venkateswaran (620, 623) and of Thatte and Ganesan (593). The intensities recorded are difficult to correlate, as they are apparently given by authors on a somewhat different scale.

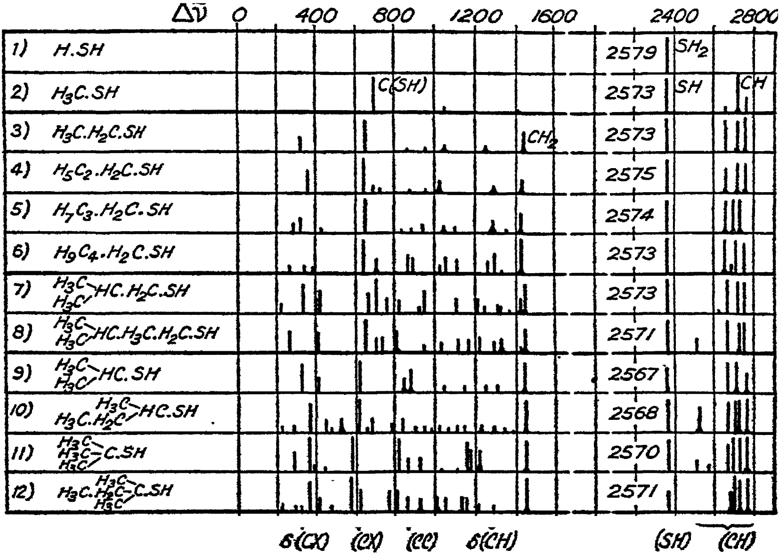


FIG. 28. Comparison spectra of some mercaptans (after Kohlrausch)

The shifts pertaining more definitely to the oscillations involving the sulfur atom are underlined. In dimethyl sulfide there is a tendency for the shifts to pair. A comparison of the scattered spectra obtained with that of diethyl ether shows that Δν̄ 441 and 845 in the ether corresponding to Δν̄ 648 and 696 in the thioether and Δν̄ 928 and 1027 occurring in the ethyl ether correspond to Δν̄ 972 and 1052 in the sulfur compound.

In dipropyl sulfide most of the lower frequency shifts are attributable to the influence of the sulfur and occur in pairs. This tendency is continued in most of the higher sulfides. The strongest characteristic shifts of allyl sulfide are Δν̄ 416, 590, and 748. Δν̄ 1206 and 1300, which are relatively weak in the other sulfides, are intensified in allyl sulfide. It is not entirely clear in the thio acids just what shifts may be ascribed to the contribution of the sulfur. Presumably they are $\Delta\bar{\nu}$ 638 and 818 in the two acids. From another point of view, however, these acids are very interesting. The carbonyl shift in thioglycolic acid is very weak and possibly a doublet $\Delta\bar{\nu}$ 1553 and 1707. In thioacetic acid $\Delta\bar{\nu}$ 1695 corresponds to the carbonyl shift. There is, however, in neither case a shift which would correspond to a S—H linkage. In view of the prominence of this shift its omission is indicative of the absence of this bond. In general it may be assumed in agreement with Venkateswaran (623) that $\Delta\bar{\nu}$ 691 and 746 are more or less characteristic of the sulfur to carbon link-

TABLE 27

The partial Raman spectra of the thioethers and thioacids

CH_3SCH_3	$C_2H_5SC_2H_5$	$C_3H_7SC_3H_7$	$[(CH_3)_2CHCH_2]_2S$	$C_4H_9SC_4H_9$	$[CH_2{=}CHCH_2]_2S$	CH_3COSH	$CH_2OHCOSH$
		290 (2)					
	318 (1)	*378* (1)			*416* (3)		
					590 (5)	459 (3)	438 (1)
691 (6)	*648* (4)	*652* (2)		*655* (3)		*638* (5)	
	696 (3)				*688* (1)		
743 (2)		*730* (2)	*731* (2)	*753* (1)	*748* (8)		
			814 (2)	*794* (1)	753 (8)	841 (2)	818 (4)
				867 (3)			
		895 (1)		892 (3)			
	972 (2)		*950* (2)		918 (2)		
	1052 (1)	*1033* (2)		*1054* (3)		1007 (2)	914 (2)
				1102 (3)	1206 (4)		
	1245 (1)			1298 (3)	1300 (6)		
1424 (1)	1453 (3)	1445 (2)	1458 (2)	1417 (4)	1405 (6)	1426 (1)	*1409* (2)
				1454 (6)	1430 (4)		
							1563 (10)
					1634 (10)	1695 (4)	
							1707 (1)
	2870 (3)	2858 (2)	2875 (5)	2873 (5)	2914 (8)		
2912 (8)	2918 (2)	2900 (4)		2914 (8)	2943 (3)	2920 (3)	
	2932 (10)	2920 (6)		2934 (5)	2978 (5)		
2984 (4)	2977 (4)	2965 (6)	2962 (3)	2960 (5)			2950 (1)
					3009 (6)		
					3084 (4)		

age. Other shifts such as Δν̄ 284, 1033, 1252, and 1335 which are variously ascribed to the linkage must be accepted with caution. While it is true that these make their appearance with increased complexity of the molecule, the appearance of any line with increased complexity is not a phenomenon solely confined to the thioethers. Most of these last-named shifts may be found as a first approximation in the hydrocarbons.

There is another type of organic sulfur compound which has been somewhat investigated and is of considerable interest. This is the class of the polysulfides. They have been investigated by Venkateswaran (623), Bonino and Manzoni-Ansidei (90), Gopala Pai (268), and Meyer (437). Results with some of the compounds investigated are in table 28. The polysulfides as well as the monosulfides show a strong frequency near Δν̄ 700. As noted in the case of sulfides with an increased complexity in the molecule there results an increased multiplicity of these sulfur frequencies. For example, in dimethyl disulfide appears Δν̄ 509; in diethyl disulfide this becomes Δν̄ 508 and 526. This appears as Δν̄ 513 in dimethyl trisulfide, but is completely absent in the ethyl derivatives. This is an anomalous behavior. There are frequencies in the polysulfides which are not far removed from those in sulfur. The Δν̄ 433 and 470 in sulfur appear as Δν̄ 446 and 489 in the trisulfide, and as Δν̄ 450 and 486 in the tetrasulfide. What significance may be attached to this is doubtful because the spectrum of sulfur is not determined in the form of S_2 or S_4. Presumably the shift for the S—S bond is near Δν̄ 500. This would give a calculated value of approximately Δν̄ 725 for a S═S linkage. This apparently is absent. Consequently it is presumed that the sulfur in the polysulfides is bound together by a single homopolar linkage.

The cyclic organic sulfur compounds which have been investigated are chiefly thiophene and its derivatives, 2-methylthiophene, 2,5-dibromothiophene, and 2,3,5-trichlorothiophene. Bonino and Manzoni-Ansidei (91) obtain Δν̄ 446 (1), 602 (3), 691 (1), 743 (2), 830 (7), 1030 (5), 1076 (5), 1356 (4), 1404 (6), 3081 (2), 3113 (4) for thiophene. Especially characteristic are Δν̄ 3113 and 3083 for the C↔H and Δν̄ 1404 to 1439. The frequencies occurring at Δν 602 (3) and 743 (2) in thiophene become Δν̄ 661 (4) and 739 (3) in 2-methylthiophene and Δν̄ 654 (4) and 704 (1) in 2,5-dibromothiophene; they are reduced to a single frequency, Δν̄ 683, in the trichloro compound. The absence of a line corresponding to a classical C═C oscillation will be discussed later.

Q. The Raman spectra of nitrates, nitrites, and nitro compounds

The organic nitrates yield as principal frequencies of the NO_3 group Δν̄ 730, 1074, 1391, and 1659. The spectrum of concentrated nitric acid yields Δν̄ 607, 667, 916, 1292, 1665, and 1685, which spectrum radically alters with dilution.

The organic nitrogen oxide derivatives have been investigated by Dadieu, Jele, and Kohlrausch (151), Dadieu and Kohlrausch (170, 173), Ganesan and Venkateswaran (242), Milone (442), Médard (429, 430), Médard and Alquier (431), Petrikaln and Hochberg (498), Ganesan and Thatte (240, 241), and Thatte and Ganesan (592). These compounds are characterized by the relative intensity of their identifying shifts. The frequencies characteristic of the NO_3, or more correctly the $O—NO_2$ group, on the average are $\Delta\bar{\nu}$ 575, 868, 1290, and 1640. These may vary somewhat from compound to compound but are easily recognizable from their intensities. In table 29 are given all except the weakest lines for

TABLE 28

Raman spectra of the polysulfides

$\begin{array}{c}C_2H_5S\\ \vert\\ C_2H_5S\end{array}$	$\begin{array}{l}CH_3S\diagdown\\ \qquad\quad S\\ CH_3S\diagup\end{array}$	$\begin{array}{l}C_2H_5S\diagdown\\ \qquad\quad\; S\\ C_2H_5S\diagup\end{array}$	$\begin{array}{r}C_2H_5—S—S\\ \vert\\ C_2H_5—S—S\end{array}$
		157 (3)	154 (1)
	184 (1)		
197 (3)		203 (3)	202 (1)
	240 (1)		
	282 (1)		
332 (2)			
372 (2)		371 (1)	
	446 (2)	439 (2)	450 (0)
	489 (3)	487 (4)	486 (6)
508	513 (3)		491 (1)
526			
644 (5)		644 (4)	644 (3)
672 (5)	700 (5)	670 (3)	665 (1)
759 (1)			
974 (4)	958 (1)	970 (2)	965 (½)
1026 (1)			
1055 (3)		1050 (2)	
	1152 (1)		
	1225 (0)	1199 (1)	
1255 (1)		1266 (1)	1254 (½)
1353 (2)	1312 (0)		
1421 (2)	1435 (3)	1418 (2)	1417 (2)
1456 (3)		1456 (2)	1448 (2)
2870 (2)		1578 (1)	2876 (1)
2924 (4)			2913 (3)
			2931 (4)
2971 (4)	2985 (2)	2970 (0)	2969 (2)
	3044 (2)		

ten organic nitrates, taken from the work of Médard (429) and of Médard and Alquier (431). It is presumed by Médard that the frequencies at $\Delta\bar{\nu}$ 1307 and 1455 pertain to the CH_2 and CH_3 groups, respectively, and those between $\Delta\bar{\nu}$ 2700 and 3047 to the C—H oscillation. Many of the frequencies observed are common to those obtained from the aliphatic alcohols and hydrocarbons. On the other hand, there are some peculiarities. The shift near $\Delta\bar{\nu}$ 1450 appears as a doublet beginning with amyl nitrate, becomes a single line in heptyl nitrate, and appears again as a doublet in the remainder of the series. The shift at $\Delta\bar{\nu}$ 1080 (5) appears only in nonyl, decyl, and dodecyl nitrates with any intensity. It is present but faint in lower homologs. The shift at $\Delta\bar{\nu}$ 1640 may be indicative of the N=O binding as the ethylenic shift is indicative of the C=C binding. Although the two lower frequencies in concentrated nitric acid are somewhat displaced, there is a general correspondence between the frequencies

TABLE 29

Raman spectra of some alkyl nitrates

CH_3NO_3	$C_2H_5NO_3$	$C_3H_7NO_3$	$C_4H_9NO_3$	$C_5H_{11}NO_3$	$C_6H_{13}NO_3$	$C_7H_{15}NO_3$	$C_9H_{19}NO_3$	$C_{10}H_{21}NO_3$	$C_{12}H_{25}NO_3$
365 (5)	385 (5)	352 (5)							
582 (7)	570 (5)	571 (5)	569 (5)	574 (5)	573 (5)	570 (5)	570 (5)	570 (5)	568 (5)
		611 (1)		616 (5)	615 (5)				
669 (5)	657 (1)		702 (5)	706 (5)					
864 (7)	864 (5)	866 (5)	848 (5)	869 (7)	869 (7)	864 (7)	864 (8)	862 (8)	861 (8)
			880 (5)						
							1080 (5)	1080 (5)	1078 (5)
1290 (10)	1285 (7)	1282 (7)	1281 (7)	1285 (7)	1283 (1)	1284 (5)	1280 (5)	1279 (5)	1279 (5)
				1315 (5)	1313 (5)		1307 (5)	1308 (5)	1307 (5)
				1392 (5)		1388 (5)			
1437 (5)					1439 (8)		1440 (5)	1441 (5)	1440 (5)
1460 (5)	1455 (5)	1454 (5)		1450 (5)		1455 (5)	1463 (5)	1464 (1)	1464 (1)
				1473 (5)	1476 (8)				
				1531 (1)		1568 (5)			
1644 (8)	1633 (5)	1635 (5)	1632 (5)	1640 (8)	1640 (8)	1632 (5)	1635 (5)	1635 (5)	1633 (5)
	2725 (1)	2739 (1)	2744 (1)	2741 (1)	2744 (1)	2730 (1)			
2839 (1)	2890 (1)	2888 (1)	2881 (1)	2881 (1)	2878 (1)	2852 (1)	2885 (5)	2885 (5)	2857 (5)
						2899 (5)	2899 (8)	2897 (8)	2895 (5)
2910 (5)			2917 (5)	2920 (7)	2916 (5)				
2968 (7)	2948 (7)	2945 (7)	2941 (7)	2949 (7)	2943 (7)	2936 (7)	2936 (5)	2933 (5)	2936 (5)
	2991 (7)	2985 (5)	2976 (5)	2980 (5)	2973 (5)	2968 (5)	2967 (5)	2963 (5)	2963 (5)
3047 (5)									

observed in this compound and those obtained from the organic O—NO_2 group. This is in contradistinction to the complete lack of agreement between the R—NO_3 frequencies and those observed in the alkali nitrates. Consequently there is a reasonable presumption that concentrated nitric acid has the ester structure HO—NO_2 in lieu of the structure HNO_3. On dilution, however, the HNO_3 frequencies are so modified that there is unquestionably a conversion to the nitrate ion identical with the alkali nitrates.

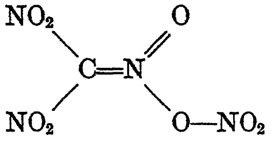
TABLE 30

Partial Raman spectra of some aliphatic nitrites and nitro compounds

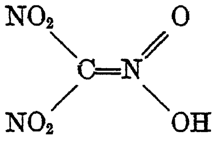
$\Delta\bar{\nu}$						
CH_3NO_2	$CH(NO_2)_3$	$C(NO_2)_4$	$C_2H_5NO_2$	$C_5H_{11}NO_2$	CH_3ONO	C_4H_9ONO
		193 (5)				
	200 (5)	227 (5)	295 (3)	255 (2)		
	374 (7)	355 (10)	389 (2)	349 (1)	364 (2)	
483 (5)	410 (8)	410 (5)	492 (5)			
					580 (4)	
657 (8)			614 (4)	603 (2)	610 (2)	605 (3)
				769 (3)		796 (2)
	837 (5)	857 (7)	875 (8)		833 (3)	833 (3)
918 (10)	942 (8)	998 (5)	995 (3)	904 (5)		
			1101 (4)	1128 (3)		1123 (2)
	$\left.\begin{matrix}1249\\1307\end{matrix}\right\}(8)$	1270 (7)				
	$\left.\begin{matrix}1309\\1366\end{matrix}\right\}(10)$	1342 (5)	1367 (7)	1342 (2)		
1376 (7)	1371 (7)		1394 (5)	1379 (5)		
1402 (7)			1447 (4)	1455 (4)	1431 (2)	1438 (6)
1560 (5)			1556 (4)	1551 (3)		
	1613 (7)	1610 (8)			1603 (3)	
		1646 (8)			1648 (8)	1640 (5)
				2873 (3)		
						2915 (5)
2968 (7)			2950 (7)	2965 (4)		2937 (3)
			2998 (3)			
3057 (1)						

There are two other nitrogen oxide derivatives of organic compounds. These are the nitro compounds with a group R—NO_2 and the nitrites with the group O—NO. Nitromethane, CH_3NO_2 (430), yields $\Delta\bar{\nu}$ 483 (5), 610 (1), 657 (8), 918 (10), 1109 (1), 1376 (7), 1402 (7), 1560 (5), 2968 (7), 3057 (1), and methyl nitrite, CH_3ONO (151), $\Delta\bar{\nu}$ 364 (2), 580 (4), 610 (2), 833 (3), 977 (0), 1431 (2), 1603 (3), 1648 (3), and 2944 (4).

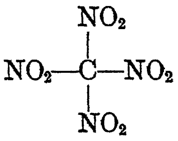
In table 30 are given the Raman spectra of some of the substituted nitromethanes and nitrites. Apparently the characteristic frequencies of the nitro group are approximately $\Delta\bar{\nu}$ 420, 1340, and 1607. In the higher homologs of the nitrites the doublet appearing between $\Delta\bar{\nu}$ 1600 to 1650 in the methyl nitrite reduces to a single frequency at $\Delta\nu$ 1640. Consequently the nitrates and nitrites have the common frequency $\Delta\bar{\nu}$ 1640, which is displaced to $\Delta\bar{\nu}$ 1590 in the nitro compounds. The nitro group possesses $\Delta\bar{\nu}$ 1376, which is 1290 in the nitrates and non-existent in the nitrites. By these strong lines alone these compounds can be easily identified. The inorganic nitrites possess $\Delta\bar{\nu}$ 696, 785, 1303 to 1330. No $\Delta\bar{\nu}$ 1600 was observed. It is to be remarked that the inorganic nitrites have been little investigated, and there is little correlation between these organic and inorganic observations. This would possibly indicate a true NO_2 group in this case rather than an O—N=O group. Médard considers the C—N linkage as varying from $\Delta\bar{\nu}$ 910 to 850 in the nitro compounds. It is believed by Médard that the structures of the nitromethanes are



and

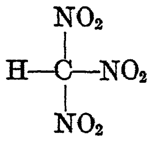


rather than



$$NO_2-\overset{NO_2}{\underset{NO_2}{C}}-NO_2$$

and



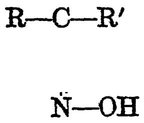
$$H-\overset{NO_2}{\underset{NO_2}{C}}-NO_2$$

Chloropicrin and bromopicrin, observed by Milone (442), yield among other lines $\Delta\bar{\nu}$ 420, 1333, and 1578 as constant frequencies. It is possible that the $\Delta\bar{\nu}$ 1575 to 1650 frequency is attributable to the C=N linkage rather than to the N=O. This will be discussed under the oximes. In N_2O the shifts are $\Delta\bar{\nu}$ 1284 and 2224, indicating a triple bond (N≡N) group and possibly an N=O group, although the N=O shift in NO is $\Delta\bar{\nu}$ 1877.

The cyclic nitro derivatives yield a strong line at $\Delta\bar{\nu}$ 1340 and $\Delta\bar{\nu}$ 1520 to 1590.

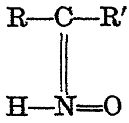
R. The Raman spectra of the oximes

It is quite apparent from the preceding discussion that the linkage between nitrogen and carbon in the form of N—C or the linkage between nitrogen and oxygen as N═O is of the same order of magnitude, at least, as the equivalent linkages between carbon and carbon, and carbon and oxygen. The problem of the N═C linkage becomes a necessity in the discussion of the oximes. Bonino and Manzoni-Ansidei (87, 88) have studied the oximes, and according to these authorities the following formulas have been proposed to represent their structure:



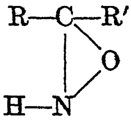
$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \\ \mathrm{\dot{N}{-}OH}\end{array}$$

1

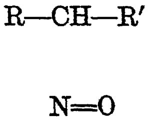


$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \Vert\\ \mathrm{H{-}N{=}O}\end{array}$$

2

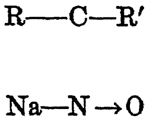


3



$$\begin{array}{c}\mathrm{R{-}CH{-}R'}\\ \\ \mathrm{N{=}O}\end{array}$$

4



$$\begin{array}{c}\mathrm{R{-}C{-}R'}\\ \\ \mathrm{Na{-}N{\rightarrow}O}\end{array}$$

5

While not entirely clarifying the problem of this structure, the Raman spectra throw some light on the subject and eliminate beyond question as possibilities some of the formulas given above.

The frequencies observed for some of the oximes studied are given in table 31. First of all, there are no frequency shifts near $\Delta\bar{\nu}$ 1300 or 1370 observed in the nitrates and nitro compounds. There is, however, the strong and constant frequency in the aliphatic ketoximes at $\Delta\bar{\nu}$ 1655 to 1665. This is appreciably higher than the corresponding frequency in the nitrates, which occurs at $\Delta\bar{\nu}$ 1635. It is natural to suppose that the C═N frequency would occur somewhere within this region. From an analogy with the ethylenic double bond one would expect that it would be a frequency less than that observed for N═O. In spite of this it would seem from the total evidence that the double-bond frequency occurring in the ketoximes corresponds to the C═N linkage. This is further substantiated by the non-concordance of the double-bond shift with any of the nitrogen oxides. On the other hand, the N═O shift as determined from the nitrogen oxides is never with a single oxygen but always with at least two oxygen atoms. Consequently the —N═O determined in this way may be somewhat lower than its ordinary position. Other evidence in favor of attributing the linkage in the oximes to a C═N rather than to a C═O is obtained from the Raman spectrum of benzalaniline, which yields $\Delta\bar{\nu}$ 1630, a shift practically identical with that observed in α-benzaldoxime. This would eliminate as possible formulas 2, 3, and 4 given above. Formula 2 is also discarded on the ground that the effect of a linkage of the type ═N═ presumably would result in a strong modification of the double-bond shift as observed in the allenes, which have been discussed, and in the isocyanates, which will be treated later. A summary of the frequencies observed for C═N is given in table 32.

In the phenyl derivatives of the oximes the C═C shift remains practically constant and the C═N shift is relatively constant for each class of compound. The aliphatic ones yield the shift near Δν̄ 1655 and the aromatic near Δν̄ 1625. However, the sodium salts of the aromatic oximes have a frequency shift which is nearly 70 wave numbers less than for the corresponding normal oximes, occurring at approximately Δν̄ 1545. This reduction is of the same order of magnitude as that occurring in the N=O shift of the nitro compounds, as compared with the same shift in the nitrites and nitrates. Bonino and Manzoni-Ansidei consider this attributable to the perturbation caused by the establishment of a semi-polar bond in both of these compounds as postulated by Sugden (581) and Sidgwick (558) and as represented by formula 5. The general problem of shared electrons and semi-polar valencies has been discussed by Noyes (477, 478). There are other lines which occur in these compounds besides the double-bond shift. The one at Δν̄ 1440 was originally supposed to be connected with the nitrogen double bond (83). Regardless of the

TABLE 31

Raman spectra of some oximes

Methyl ethyl ketoxime	Methyl propyl ketoxime	Methyl heptyl ketoxime	α-Benzaldoxime	Na benzaldoxime
			308(2)	
351(3)				
	377(2)	368(2)	371(2)	
411(3)				
			452(1)	473(3)
525(3)	531(3)	578(2)	511(1)	518(3)
			618(3)	
606(5)	600(3)	648(2)		
			746(1)	
			788(1)	
802(5)	814(4)	818(4)		
928(3)	901(1)	880(3)	858(2)	
993(4)	953(1)	947(4)	996(5)	996(4)
1082(4)	1078(2)	1003(4)	1020(2)	
		1188(4)	1180(3)	1176(3)
			1207(5)	1205(4)
1261(3)		1295(5)	1285(2)	
1426(5)	1441(5)	1430(5)	1433(2)	1440(2)
			1603(5)	1547(5)
1663(5)	1658(5)	1655(5)	1628(5)	1589(5)
	2858(3)	2862(3)		
2913(3)				
2948(3)	2931(3)	2928(4)		
			3052(3)	3046(3)

fact that this occurs in the aromatic compounds it is more likely that this is connected with the CH_2 group. It is probable that the generally accepted formula to depict the structure of the oximes is the correct one.

S. The Raman spectra of cyano compounds and their derivatives

This class of compounds is of particular interest because it illustrates the triple linkage between carbon and nitrogen. It will be recalled that the monosubstituted acetylenes gave $\Delta\bar{\nu}$ 2120 and the disubstituted acetylenes $\Delta\bar{\nu}$ 2235 and 2305 for the $C\equiv C$ linkage. The simplest cyanide is HCN. According to Bhagavantam (44) the shifts obtained are $\Delta\bar{\nu}$ 2076, 2097, and 2122, of which the middle shift is the strongest. Dadieu (145, 148) obtained $\Delta\bar{\nu}$ 2094 and 2062. The 2062 shift was attributed to the isomer HNC. Other organic and inorganic nitriles have been investigated by Dadieu (145, 148), Dadieu and Kohlrausch (163, 165, 166, 167, 169, 172), Cheng (125), Kastler (330), Lechner (400), Venkateswaran (625), Kopper and Pongratz (371), Hemptinne and Wouters (306), Pal and Sen Gupta (485), Petrikaln and Hochberg (500, 501), and Howlett (320). Beginning with acetonitrile and ending with isocapronitrile there is complete agreement between observers that the characteristic shift of these compounds for this linkage is $\Delta\bar{\nu}$ 2245 (6) as an average. This is not far removed from the frequency observed in the acetylenes for the triple-bond linkage. This is further evidence of a rough correspondence of the strength of the normal bond between carbon and carbon, and carbon and nitrogen. One of the earliest demonstrations of the utility of the Raman spectra method in determining the structure of organic compounds was its application to the isonitriles. The derivatives investigated were the methyl and ethyl isonitriles. For these compounds Dadieu obtained

TABLE 32

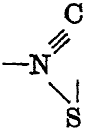
Characteristic $C=N$ *shifts*

COMPOUND	$\Delta\bar{\nu}$	
	$C=N$	$C=C$
Methyl ethyl ketoxime	1663	
Methyl propyl ketoxime	1658	
Methyl butyl ketoxime	1655	
Camphor *O*-methyloxime	1651	
α-Benzaldoxime	1628	1603
Sodium α-benzaldoxime	1547	1589
Acetophenone oxime	1623	1595
Sodium acetophenone oxime	1548	1586
Sodium *o*-chlorobenzaldoxime	1541	1583

$\Delta\bar{\nu}$ 2161 (5) and 2146 (7), respectively. This shows clearly that there exists a triple bond between the carbon and nitrogen in the nitriles and isonitriles. In the case of the latter, however, the frequency is reduced by roughly 100 wave numbers. This is approximately the magnitude of shift alteration in going from dimethylacetylene to methylacetylene. Consequently this behavior is by no means anomalous. The only wide departures from these two characteristic shifts are in cyanogen (501), which yields $\Delta\bar{\nu}$ 2335, and the inorganic cyanides, which yield $\Delta\bar{\nu}$ 2080 comparable with the shift observed in hydrogen cyanide. As Dadieu and Kohlrausch (175) have pointed out, however, this lower shift is confined to those compounds which are dissociated readily. In the complex cyanides, such as potassium ferrocyanide, and in mercury cyanide, the shift appears near $\Delta\bar{\nu}$ 2150. The inorganic cyanides have been treated in detail by Hibben (311).

Cheng (125) has studied the chlorine derivatives of acetonitrile. In going from chloroacetonitrile to trichloroacetonitrile the frequency remains unchanged. The substitution of a phenyl group, however, will reduce the average $\Delta\bar{\nu}$ 2250 shift by 25 wave numbers, so that in benzonitrile and tolunitrile or dimethylbenzonitrile the shift remains $\Delta\bar{\nu}$ 2225. Cheng believes there is a shift characteristic of the C—CN group which occurs between $\Delta\bar{\nu}$ 150 and 187 in all these compounds.

Hemptinne and Wouters (306) have investigated the nitrile derivatives of the unsaturateds and obtained $\Delta\bar{\nu}$ 2235 to 2255. The ethylenic shift in vinylnitrile is $\Delta\bar{\nu}$ 1629, in crotononitrile $\Delta\bar{\nu}$ 1645, and in isocrotononitrile $\Delta\bar{\nu}$ 1627.

1. Thiocyanates and isothiocyanates. Aside from a differentiation in the structure of nitriles and isonitriles it has also been possible to investigate the thiocyanates and isothiocyanates. Dadieu, for example, observed $\Delta\bar{\nu}$ 2145 (6) in methyl thiocyanate, and $\Delta\bar{\nu}$ 2152 (7) in ethyl thiocyanate. In the ethyl isothiocyanate was observed $\Delta\bar{\nu}$ 2106 (3) and 2182 (2), in isobutyl isothiocyanate $\Delta\bar{\nu}$ 2100 (3) and $\Delta\bar{\nu}$ 2172 (3), and in phenyl isothiocyanate, $\Delta\bar{\nu}$ 2100 (3) and 2172 (3). The constitution of the isothiocyanates was formerly indicated by —N=C=S. It has been suggested (175) that this constitution should be  or (87) $R-\overset{+}{N}\equiv C-S$. In comparing the two isomers, C_2H_5SCN and C_2H_5NCS, both show strong shifts near $\Delta\bar{\nu}$ 630 and $\Delta\bar{\nu}$ 942. There is no shift in the region corresponding to the linear vibration of the ethyl group against the SCN or NCS radical which is markedly different in the two isomers. The isothiocyanate compound shows $\Delta\bar{\nu}$ 1069 (6) and 1340 (3) not present in the ethyl thiocyanate. On comparing acetonitrile with methyl isonitrile, little difference appears in the spectra other than that attributable to the C=N linkage.

It will be recalled that the C—S shifts in the mercaptans and thioethers occurred near $\Delta\bar{\nu}$ 650 and 733. All inorganic thiocyanates exhibit a frequency at approximately $\Delta\bar{\nu}$ 745. This is reflected in both the RNCS and RSCN compounds by a strong shift varying from $\Delta\bar{\nu}$ 626 to 690.

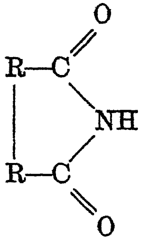
2. *Isocyanates.* The isocyanates have been considered to have the structure R—N=C=O. This structure has an air of familiarity and is more than reminiscent of the allenes (R—C=C=R). The allenes show no C=C shift at $\Delta\bar{\nu}$ 1640 but show a strong displacement at $\Delta\bar{\nu}$ 1100. The isocyanates (145, 371) exhibit no shift at $\Delta\bar{\nu}$ 1650 for C=N or C=O, but have a medium strong shift at $\Delta\bar{\nu}$ 1409 (5) and 1434 (5) in the methyl and ethyl cyanates respectively; $\Delta\bar{\nu}$ 1421 (4) in isopropyl isocyanate, $\Delta\bar{\nu}$ 1440 (5) and 1510 (4) for phenyl isocyanate, and $\Delta\bar{\nu}$ 1438 (5) and 1513 (4) for α-naphthyl isocyanate. This is excluding the $\Delta\bar{\nu}$ 1450 shifts attributable to C—H, which also occur in the aliphatic compounds, and the C=C shift at $\Delta\bar{\nu}$ 1590, which is present in the aromatic compound. The perturbating effect of adjacent double bonds seems to reduce seriously the frequency of the C=N and C=O linkages. As the mass factor is not greatly different from that in the allenes this reduction must be concomitant with the change in force.

3. *Summary.* Thus far it has been observed that all the carbon-nitrogen and nitrogen-oxygen compounds have distinct shifts. The N=O inner vibration appears at $\Delta\bar{\nu}$ 1565 in the R—NO_2 compounds, $\Delta\bar{\nu}$ 1640 in the R—O—NO_2 compounds, and $\Delta\bar{\nu}$ 1640 in the R—O—NO compounds. From the oximes it is deduced that the C=N inner vibration is $\Delta\bar{\nu}$ 1650 and from the nitriles the C=N vibration is $\Delta\bar{\nu}$ 2150. This is subject to some variation dependent on the adjacent groups. There is no possibility of a quadruple bond in the isonitriles. The C=N=O type of linkage yields $\Delta\bar{\nu}$ 1440 (5) as a modified frequency. The C—S linkage in the thiocyanogens occurs near $\Delta\bar{\nu}$ 626 to 690. The N≡CS and SC≡N inner vibrations for the carbon-nitrogen groups are $\Delta\bar{\nu}$ 2100 and 2175 for the first of these last two types of linkage, and $\Delta\bar{\nu}$ 2150 for the second. Up to this point the C—N linkage can only be estimated from the isonitriles, isothiocyanates, or nitro compounds. Although this is a somewhat precarious approach in the case of the C—N linkage, $\Delta\bar{\nu}$ 910 to 930 would seem a possible estimate. This is only slightly higher than the C—C inner vibration. Bonino and Cella (83) consider the C—N vibration to be $\Delta\bar{\nu}$ 1042. An examination of the amines may shed some light on this question.

Just as the C═C oscillation may occur at $\Delta\bar{\nu}$ 1500 under special circumstances (cyclopentadiene), so may the C═N shift appear at a frequency much lower than its normal amount. This will be discussed later under heterocyclic compounds.

T. The Raman spectra of amines, amides, and imido compounds

1. Amines. The amines have the general formula RNH_2, the amides $RCONH_2$, and the imido compounds



and are all represented in Raman spectra.

There are two inorganic compounds which will help to define the N—H linkage. These are NH_3 and NH_2—NH_2. Ammonia yields $\Delta\bar{\nu}$ 3210 (3), 3310 (5), 3380 (3), hydrazine yields $\Delta\bar{\nu}$ 904 (1), 1112 (1), 3212 (2), 3272 (2), 3340 (2), and phenylhydrazine yields $\Delta\bar{\nu}$ 3366 (2) for its characteristic linkage, from the observations of Pal and Sen Gupta (485), Sutherland (582), and Imanishi (326).

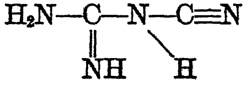
As to methylamine there is some discrepancy between observers. Venkateswaran and Bhagavantam (626) observe $\Delta\bar{\nu}$ 1033 (2), 2870 (2), 2955 (2), 3301 (2) in the liquid, and Dadieu and Kohlrausch (168) $\Delta\bar{\nu}$ 1038 (4), 1470 (3), 2901 (4), 2965 (5), 3319 (5), and 3378 (3) in solution. In the higher homologs the N—H shift remains near $\Delta\bar{\nu}$ 3320 and 3375. Both shifts are reduced somewhat in ethylenediamine. The disubstituted amines (173) R_2NH yield only one frequency near $\Delta\bar{\nu}$ 3320.

So far as a C—N frequency is concerned this occurs at $\Delta\bar{\nu}$ 1038 in methylamine. But, as has been shown in the alcohols and hydrocarbons, the group oscillation in the first member of a series gradually diminishes. In ethylamine this becomes $\Delta\bar{\nu}$ 880 and in propylamine $\Delta\bar{\nu}$ 868. The cyclic hydrocarbons may have an increased C—H frequency, namely, $\Delta\bar{\nu}$ 3360 (3) and 3420 (2) in aniline (176). This augmentation is because of the adjacent phenyl group. This is shown by the fact that in benzylamine the frequency has returned to normal. Benzalaniline gives $\Delta\bar{\nu}$ 1637 for the C═N but no recorded shift for N—H. Practically all the substituted benzenes exhibit a frequency near $\Delta\bar{\nu}$ 1030, so that the presence of this shift is not to be correlated necessarily with the nitrogen influence even though it is present in the aniline derivatives. Ganesan and Thatte (239) observe that all the benzene lines appear in aniline. In xylidine no line appears near $\Delta\bar{\nu}$ 3432.

2. Amides. Formamide according to Thatte and Joglekar (594) yields $\Delta\bar{\nu}$ 394 (1), 605 (1), 726 (2), 1109 (1), 1306 (1), 1382 (2), 1675 (1), 3340 (1), and acetamide $\Delta\bar{\nu}$ 377 (1), 571 (1), 870 (3), 1400 (1), 1608 (1), 2940 (2), and 3375 (1). These observations were made on the liquid compounds. They are not in too great agreement with Dadieu and Kohlrausch (162, 176) and Kohlrausch and Pongratz (366), taken, however, under different conditions. In the higher homologs of formamide have been observed (366) two carbonyl frequencies, $\Delta\bar{\nu}$ 1606 (2) and 1664 (3). The frequency corresponding to the aliphatic carbonyl shift ($\Delta\bar{\nu}$ 1710) is appreciably lowered by the NH group. From the benzamide (594) appear $\Delta\bar{\nu}$ 1702 (1) for C=O, and $\Delta\bar{\nu}$ 3360 for the N—H. Comparing this to benzophenone ($\Delta\bar{\nu}$ 1651 (4)) shows a notable increase in frequency in the amide and a decrease in intensity. Acetanilide yields only $\Delta\bar{\nu}$ 1600 (10). The reason for the diminution in the frequency is not entirely clear.

3. Imides. Succinimide has been found (369) to give $\Delta\bar{\nu}$ 1760 (4), 3332 (1) for the C=O and N—H frequencies, while potassium phthalimide yields $\Delta\bar{\nu}$ 1575 (2), 1599 (3), and $\Delta\bar{\nu}$ 1602 ($\frac{1}{2}$). Their allocation is indeterminate.

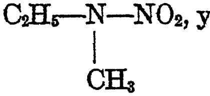
4. Other compounds. The compound dicyanodiamide (176)



$$H_2N—\underset{\underset{NH}{\|}}{C}—\underset{\diagdown H}{N}—C\equiv N$$

gives $\Delta\bar{\nu}$ 655 (1), 927 (2), 1648 (1), 2156 (3), 2195 (3), which aids in establishing the C=N frequency.

Methyl nitramine, $C_2H_5—\underset{\underset{CH_3}{|}}{N}—NO_2$, yields among other shifts $\Delta\bar{\nu}$ 1563 (2) and $\Delta\bar{\nu}$ 1388 (1) of possible significance.



Urea, H_2NCONH_2, according to Pal and Sen Gupta (485), shows $\Delta\bar{\nu}$ 830, 1002, 1162, 3226, and 3374; Kohlrausch and Pongratz (366) obtained $\Delta\bar{\nu}$ 525 (2), 585 (1), 1000 (8), 1157 (1), 1593 (2), 1655 (0), 3218 (1), 3383 (3), and 3462 (2). Liquid urea was observed by Thatte and Joglekar (594) to have $\Delta\bar{\nu}$ 1008 (2), 1180 (1), 3230 (1), and $\Delta\bar{\nu}$ 3374 (1).

There is doubt concerning any frequencies assignable to C=O in this compound, but the C—N frequency would seem to be in the neighborhood of $\Delta\bar{\nu}$ 1000. Its structure as written above seems inconsistent with the observations.

U. The Raman spectra of some heterocyclic compounds

1. Furans. The first of the heterocyclic compounds to be considered will be the five-membered rings with oxygen as the odd atom. In this series furan has been the most investigated. This has been studied by Bonino (69, 70), Bonino and Manzoni-Ansidei (91), Glockler and Wiener (257), Médard (426), and Prévost, Donzelot, and Balla (517). It will be remembered that cyclopentadiene gave $\Delta\bar{\nu}$ 1500 (5) in contrast to $\Delta\bar{\nu}$ 1615 (7) for cyclopentene. Since furan is structurally somewhat similar to cyclopentadiene, it is to be expected that any ethylenic shift in this compound would be especially low, which is indeed the case. The observed ethylenic shift is of the order of $\Delta\bar{\nu}$ 1486, as obtained by Glockler and Wiener (257). This was attributed by them to the furan ring. The C—H shift in furan and its derivatives occurs at approximately $\Delta\bar{\nu}$ 3155, so far as the ring hydrogen is concerned. This is considerably in excess of the same type of shift observed in other cyclic compounds containing only carbon in the ring, although there are instances where an occasional very weak shift may equal or exceed this amount. This shift also appears in other heterocyclic five-atom rings including thiophene, although it may be somewhat displaced. The derivatives of furan have been studied by Bonino and Manzoni-Ansidei (91), Glockler and Wiener (257), and Matsuno and Han (422). The results are indicated in table 33 for furan and three typical derivatives. The data given in this table are taken from the work of two of the above-named authors (257, 422). The work of Matsuno and Han is the more complete, so that the absence of lines in the first two compounds as compared with the rest is not always significant. There is one point which stands out strikingly, namely, on the introduction of a side chain to the ring the ethylenic shift is augmented at times by as much as 150 wave numbers, although it is not too certain to what mode of oscillation this shift may be assigned. In 2-methylfuran, for example, instead of $\Delta\bar{\nu}$ 1486 observed in furan, the double-bond frequency becomes either $\Delta\bar{\nu}$ 1510 or 1605. The augmentation is independent of the constitution of the side chain, which may contain an alcohol, aldehyde, or ester group. In practically all cases there appear doublet shifts connected with the ethylenic linkage. In addition to the ring double-bond shift there may appear ethylenic or carbonyl shifts if side chains containing these bonds are added to the furan nucleus. In the case of the aldehyde derivatives there appear two, $\Delta\bar{\nu}$ 1668 and 1688. Both of these frequencies were observed by Kohlrausch, Pongratz, and Seka (369) and by Matsuno and Han, but not by Glockler. In the esters appear $\Delta\bar{\nu}$ 1721 to 1745 of the carbonyl frequencies, depending on the ester group. Consequently it is to be noted that the carbonyl frequency is increased by the presence of the furan group. There is also present a shift which remains fairly constant near $\Delta\bar{\nu}$ 1000, which might possibly be attributable to the C—O linkage. Matsuno and Han have discussed the attribution of the frequencies to the various derivatives. The lines corresponding to $\Delta\bar{\nu}$ 888, 1088, and 1390 are found in most five-atom rings. They believe that $\Delta\bar{\nu}$ 1507 and 1605 are characteristic of a furan derivative containing CH_2 in the side chain. The α-derivatives of furan give $\Delta\bar{\nu}$ 1460 and 1507, which are not assigned to the transverse vibration of the hydrogen. These

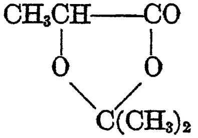
TABLE 33

Raman spectra of some furans and derivatives

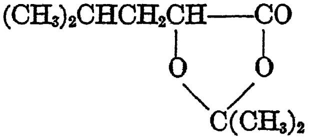
Furan	2-Methylfuran	2-Furaldehyde	Methyl α-furoate
		172	170 (2)
	253 (5)		233 (5)
	343 (3)		395 (4)
483		497	443 (3)
		581	
604	626 (3)	624	602 (1)
	654 (6)		618 (2)
735	718 (1)	758	770 (3)
	796 (1)		798 (6)
857	883 (3)	878	888 (6)
990	917 (4)	929	911 (5)
			922 (8)
	1018 (3)	1021	1019 (6)
1058 (3)	1084 (8)	1078	1081 (6)
1139	1147 (3)	1156	1122 (5)
	1215 (4)	1212	1172 (4)
	1233 (3)		1236 (5)
	1376 (3)	1378	1307 (4)
1381 (5)	1386 (9)		1390 (8)
1486 (7)	1453 (4)	1467 (10)	1478 (10)
	1510 (10)		
	1605 (6)	1567 (8)	1572 (5)
		1677 (10)	1583 (6)
		1688 (8)	
			1726 (8)
		2181	
	2745 (2)		
	2883 (3)		2845 (1)
	2928 (7)		
	2955 (2)		2956 (5)
	3119 (6)	3129	3122 (4)
3165 (3)	3153 (4)		3155 (2)

frequencies are associated with the furan ring. It is believed that the double-bond formula for these compounds is more probable than the centric formula.

2. Other oxygen rings. There are other types of heterocyclic compounds involving oxygen which are somewhat analogous to an anhydride. It has been pointed out that the anhydrides yield shifts between $\Delta\bar{\nu}$ 1775 and 1845. The anhydrides are generally ring compounds bound together through an oxygen. The shift referred to is the carbonyl shift of the oxygen, which does not enter into the ring structure. Ôeda (479) has investigated acetone lactic acid and acetone leucic acid having the formulas:



Acetone lactic acid



Acetone leucic acid

These yield $\Delta\bar{\nu}$ 1790 (5) and 1787 (5) for the lactic and leucic acid derivatives, respectively. These two compounds, therefore, behave like any other anhydride, but were included among the polycyclic compounds because of their peculiar cyclic structure. Although these are five-membered rings they show no shift in excess of $\Delta\bar{\nu}$ 1450 which can be attributed to the transverse hydrogen vibration. The maximum C—H line is $\Delta\bar{\nu}$ 2994, so that the ring hydrogen does not differ materially from that observed in cyclopentane.

Dioxane, investigated by Villars (630) and Wolkenstein and Syrkin (652), exhibits no peculiarities, the principal frequencies being the usual C—H ones and a relatively strong shift in $\Delta\bar{\nu}$ 837 (4).

3. Pyrroles. The pyrroles have been studied extensively by Bonino and Manzoni-Ansidei (89, 93) and Bonino, Manzoni-Ansidei, and Pratesi (95, 96). The pyrroles, like the furans, are five-atom rings containing an odd atom. The spectra which they exhibit have many similarities. As in the case of furan, pyrrole exhibits an exceedingly low ethylenic shift if any. The only frequency displacement between $\Delta\bar{\nu}$ 1140 and 3073 occurs at $\Delta\bar{\nu}$ 1377, a shift which occurs in slightly modified form in every derivative of the pyrroles and the furans. While this may be connected indirectly with the C—N linkage as shown by $\Delta\bar{\nu}$ 1367 in the nitro compounds, it is doubtful. The strongest shift occurring in pyrrole is at $\Delta\bar{\nu}$ 1140. This does not appear in its derivatives, with the possible exception of acetylpyrrole. This would apparently indicate a structure reminiscent of the allenes, where the double bonds are attached to the same

TABLE 34

Raman spectra of some pyrroles

Pyrrole	2-Methyl-pyrrole	2,5-Dimethyl-pyrrole	1-Methyl-pyrrole	1-Phenyl-pyrrole	1-Acetyl-pyrrole	2-Acetyl-pyrrole	2-Pyrrole-aldehyde	Tetra-chloro-pyrrole
								151 (3)
								166 (1)
	257 (4)	266 (4)		283 (3)				
		297 (3)		286 (2)				
	338 (2)	393 (1)	354 (1)	409 (1)	405 (1)			393 (2)
		485 (1)		442 (1)				
					544 (1)		502 (2)	
	596 (½)	603 (2)	607 (1)	619 (2)				
		623 (1)						
641 (2)	648 (6)	649 (1)	660 (4)		644 (1)			
		690 (3)	688 (2)	690 (3)				691 (1)
706 (1½)	710 (1)							
	782 (2)	765 (1)		758 (2)				
828 (1)			813 (2)					
852 (1)	881 (4)		868 (2)		859 (2)		869 (2)	
	953 (3)			916 (2)	914 (2)	929 (4)		
	973 (2)	991 (5)	962 (2)	962 (2)	967 (0)		954 (3)	
				1001 (5)				
				1022 (1)	1027 (0)	1045 (3)		
1035 (½)		1034 (5)	1054 (4)	1047 (3)				
1078 (½)	1089 (6)		1084 (4)		1082 (0)		1087 (4)	
				1122 (2)				
1140 (8)				1141 (1)	1132 (4)			
				1158 (3)				
				1175 (3)				
		1187 (1)		1197 (0)				
	1230 (5)	1258 (5)		1254 (3)				
			1283 (6)	1297 (1)				
				1333 (8)				
1377 (3½)	1381 (1½)	1367 (3)	1380 (7)	1395 (4)	1382 (3)	1367 (3)	1350 (5)	1383 (3)
	1435 (4)		1415 (2)	1421 (3)		1406 (4)	1400 (3)	
	1469 (5)	1458 (3)			1468 (3)			1472 (4)
		1514 (8)	1504 (3)	1501 (2)				
				1522 (4)				
	1571 (1½)	1605 (1)		1602 (8)				
				1620 (0)		1636 (5)	1645 (5)	
					1711 (4)			
			2819 (1)					
	2865 (3)							
		2902 (3)			2915 (2)			
	2918 (4)	2927 (3)	2942 (2)					
		2977 (1)				2967 (2)		
3073 (1)				3073 (3)				
		3107 (2)	3103 (2)	3117 (2)				
3123 (3)	3120 (4)		3130 (3)	3147 (2)	3135 (3)		3126 (1)	
3380 (2)	3378 (3)	3379 (1)						

carbon atom. On substitution, however, the double-bond linkage appears at $\Delta\bar{\nu}$ 1571 and 1605 or $\Delta\bar{\nu}$ 1469 and 1514. This doubling of the double-bond linkage, if this indeed can be attributed to that, depends upon whether the substitution is in the ring or on the nitrogen atom. When the substitution takes place on the nitrogen atom the spectrum is simpler. These results, summarized in table 34, are based on the observations of Bonino, Manzoni-Ansidei, and Pratesi (96). The carbonyl shifts observed in the carbonyl derivatives of pyrrole are slightly elevated from the normal position. The shift at $\Delta\bar{\nu}$ 3380 is consistent with the H—N linkage. Its absence in 2-acetylpyrrole and 2-pyrrolealdehyde is not entirely clear, although there may be some coupling with the carbonyl group. Bonino and his coworkers assume that $\Delta\bar{\nu}$ 1550 is associated with a central vibration somewhat analogous to that connected with the centric formula.

In many cases the determination of characteristic Raman lines in organic compounds is difficult, particularly those pertaining to the compound as a whole. With these five-membered heterocyclic rings, however, the difficulty seems to be not one of determining characteristic Raman lines, which are strong and moderately easy to secure, but of interpreting them after they are obtained. It is quite evident that these compounds are very different in their constitutional structure from the six-membered rings.

4. Furazans, oxdiazoles, and azoximes. These compounds are heterocyclic five-membered rings, and are somewhat related to the furans and pyrroles. They have been investigated by Milone (443) and Milone and Müller (446). All these compounds contain C═N linkages, and exhibit the same peculiarities as observed with the other cyclic compounds of this type.

The C═N shift in 3,4-dimethylfurazan occurs presumably at $\Delta\bar{\nu}$ 1461 (3). This does not entirely eliminate $\Delta\bar{\nu}$ 1396 (3). It may be argued that the former of these shifts is attributable to the methyl group. However, in 3,4-diphenylfurazan $\Delta\bar{\nu}$ 1448 and 1489 also appear. Furazan itself unfortunately has not been studied. The compound 3-methyl-4-phenylfurazan exhibits a number of frequencies in the region which could be assigned to double-bond frequencies. Of these $\Delta\bar{\nu}$ 1598 is attributable to the C═C in the benzene ring. In all the compounds involving a link between the nitrogen and oxygen atoms there is a shift near $\Delta\bar{\nu}$ 1300 to 1320, which occurs strongly in the ester form of the nitrates but not in the nitrites. A shift near $\Delta\bar{\nu}$ 2930 appears in all the compounds.

Most remarkable is the hydrogen shift occurring at $\Delta\bar{\nu}$ 3217 or higher. This is nearly in the region of the N—H characteristic linkage and may indicate some kind of tautomerism. This is further indicated by the presence of $\Delta\bar{\nu}$ 3075, which is characteristic of a hydrogen attached to C═C and is present even in the furazan and oxdiazole derivatives which do not contain a phenyl group.

The aliphatic oxdiazoles are particularly characterized by the shift of $\Delta\bar{\nu}$ 1579, in contrast to the much lower frequency observed with the aliphatic furazans. The aromatic substituted oxdiazoles, furazans, and azoximes exhibit a very similar group of lines falling between $\Delta\bar{\nu}$ 1440 and 1600. The oxdiazoles are noted by the absence of a line near $\Delta\bar{\nu}$ 1300, as has been mentioned.

TABLE 35

The Raman spectra of some furazans, oxdiazoles, and azoximes

3,4-Dimethylfurazan	2,5-Dimethyloxdiazole	3-Methyl-4-phenylfurazan	2-Methyl-5-phenyloxdiazole	5-Methyl-3-phenylazoxime	3-Methyl-5-phenylazoxime
289(1)		283(1)			
649(1)	613(1)	621(1)	629(1)	635(1)	632(2)
709(2)					958(1)
964(1)	923(1)	998(2)	991(1)	989(2)	982(1)
	1043(1)		1030(2)	1020(1)	1036(2)
				1055(1)	1069(1)
	1108(2)		1102(2)		
		1168(2)	1175(2)		1183(2)
1308(2)		1278(1)		1305(2)	1320(1)
1396(3)					
1461(3)	1438(3)	1451(3)	1442(2)	1439(2)	1463(2)
		1502(2)	1482(3)	1483(2)	1499(2)
		1546(3)	1546(3)	1541(3)	1559(3)
	1579(3)	1598(3)	1591(2)	1576(2)	1601(2)
2938(2)	2957(2)	2936(2)	2919(2)	2928(2)	2940(1)
3070(1)	3082(1)	3083(2)	3071(2)	3065(2)	3091(2)
		3190(1)	3182(1)	3178(1)	
3217(1)					3204(1)
	3349(1)				

All these results are indicated in table 35. It is particularly interesting to note the quite different spectra of the two isomeric azoximes.

5. Pyridines, quinolines, and allied compounds. Piperidine is a saturated heterocyclic compound of the type C_6, and consequently its Raman spectrum bears a close resemblance to that of cyclohexane (568). The shifts $\Delta\bar{\nu}$ 3307 and 3339 are attributed to the well-established N—H frequency. Pyridine has received considerable attention (75, 129, 359, 379, 480, 498, 621, 625, 645). Its spectrum is similar to benzene. The =C—H shift occurs at $\Delta\bar{\nu}$ 3054 and the C=C (or C=N) at $\Delta\bar{\nu}$ 1571, which is lower than the equivalent shift in benzene by about 15 wave numbers. The strongest frequency arising from a symmetrical ring oscillation occurs at $\Delta\bar{\nu}$ 992 identical with that observed in benzene. A weak shift at $\Delta\bar{\nu}$ 1379 (1) appears. Pyridine hydrochloride (379) yields $\Delta\bar{\nu}$ 3103 in place of 3054 and two new lines at 1253 (1) and 1563 (0). Substituted pyridines have been examined by Bonino and Manzoni-Ansidei (89). The compound 2-methylpyridine (α-picoline) differs from β-picoline in the lower frequency brackets. Both yield $\Delta\bar{\nu}$ 1373 (2), 1570 (2), 1599 (2), and 3052. Quinoline yields among other shifts $\Delta\bar{\nu}$ 1369 (6), 1388 (2), 1428 (3), 1568 (4), 1589 (1), 3011 (1), 3062 (3); isoquinoline yields $\Delta\bar{\nu}$ 1379 (7), 1427 (2), 1458 (2), 1496 (1), 1554 (2), 1582 (2), 1622 (1), 3020 (3), 3058 (3).

The methylindoles, peculiarly enough, exhibit no N—H shift. This is probably because of a lack of recording rather than a real absence. The double-bond shifts vary considerably with the position of the substituent groups. For 2-methylindole these shifts are $\Delta\bar{\nu}$ 1554 (3), 1588 (2), 1615 (1); for 3-methylindole $\Delta\bar{\nu}$ 1560 (2), 1577 (1), 1610 (1); for 7-methylindole $\Delta\bar{\nu}$ 1507 (2), 1600 (1). Notwithstanding the careful work of Bonino and Manzoni-Ansidei on these compounds and their derivatives, no general conclusion can be drawn at this time in regard to the complete significance of these Raman frequencies. It does not seem reasonable, however, that the C═N shift can be assigned to $\Delta\bar{\nu}$ 1433 to 1480 in the pyridine type of compounds, as noted by Bonino and Cella (83), except under such conditions that no other assignment is possible.

6. Summary. It may be generally concluded that the C═N characteristic frequency in the non-cyclic compounds is near $\Delta\bar{\nu}$ 1640 to 1655, but in the multiple bond system of the allenic type this may be reduced by more than 150 wave numbers. In the cyclic compounds the C═N frequency is considerably less than in the non-cyclic compounds. If the rings are six-membered and have a multiple bond system this shift may occur near $\Delta\bar{\nu}$ 1575. The five-membered rings exhibit a very reduced C═N shift just as the C═C shift is reduced in the C_5 cyclic or heterocyclic compounds. The double bonds in these heterocyclic compounds are very sensitive to substitution. This is not unusual as it is to be remembered that even the transition from cyclopentene to methylcyclopentene causes an augmentation in the C═C shift of 45 wave numbers; from cyclohexene to methylcyclohexene an increase of 25 wave numbers; from cyclopentadiene to cyclopentene 115 wave numbers, and finally in the substituted pyrroles the C═C shift appears at approximately $\Delta\bar{\nu}$ 1515 for the strongest component of a doublet but varies considerably with substitution. The oxdiazoles, furazans, and azoximes have a C═N shift, which is probably near $\Delta\bar{\nu}$ 1540 but also varies over a considerable range. The doubling of the double-bond shifts in this region for these last few compounds probably owes its origin to the lack of symmetry.

The C↔N vibration is more difficult to determine. It may apparently vary from $\Delta\bar{\nu}$ 930 to 1000 in the amines and isonitriles to near $\Delta\bar{\nu}$ 970 in the pyrroles, although this is also somewhat approximate. So far as the N—O is concerned the furazans, azoximes, and oximes would indicate a shift between $\Delta\bar{\nu}$ 1000 and 1078 as characteristic. Nevertheless the shift near $\Delta\bar{\nu}$ 1300 is also constant in these compounds. In hydroxylamine hydrochloride the N—OH shift has been noted by Hibben (315) to be about $\Delta\bar{\nu}$ 1050, consequently the $\Delta\bar{\nu}$ 1000 region is favored for this shift.

V. Metallo compounds

Metallo derivatives of the hydrocarbons have a useful significance. If the mass of the metallic component is sufficiently great, then it is not difficult to delineate the contributions of the radical.

Some of the earliest metallo derivatives determined were the alkyl magnesium halides, studied by Cleetin and Dufford (129). The ether solution of these compounds shows $\Delta\bar{\nu}$ 1076 for methylmagnesium iodide and 1131 for methylmagnesium bromide. These do not of course represent the complete spectra. Nickel carbonyl, according to Duncan and Murray (210), yields (on a scale of 100 for intensity) $\Delta\bar{\nu}$ 82 (100), 382 (20), 463 (8), 601 (4), 718 (0), 833 (2), 872 (2), 913 (2), 1609 (2), 2043 (30), 2132 (5), and 2223 (1). It is possible that this molecule has a structure in which all the atoms lie in a plane. The carbonyl frequencies are more in accord with those observed for C≡O than the ordinary carbonyl structure. Calculations of the Ni—CO bond yield 2.4×10^5 dynes cm.$^{-1}$ for the force constant. The phenyl metallo derivatives have been studied by Donzelot and Chaix (207). Mercury diphenyl yields $\Delta\bar{\nu}$ 158, 210, 651, 704, 998 (8), 1024, 1574 (8), 3049, and selenium diphenyl $\Delta\bar{\nu}$ 175 (5), 201 (5), 249 (1), 318 (8), 612 (5), 668 (5), 999 (10), 1021 (8), 1067 (1), 1087 (8), 1157 (5), 1180 (1), 1325 (1), 1577 (7), 3054 (7), 3155 (1), 3207 (1). The low frequency shifts are, as to be expected, notably reinforced.

Several alkyl metallo derivatives have been investigated by Gopala Pai (269). These results, together with the data on lead tetramethyl of Duncan and Murray (210), are given in table 36. In this table, as occasionally in others, it has been necessary to correct different coworkers' estimates of intensities to a common denominator. A few weak lines estimated by Duncan and Murray as 1/100 of the intensities of the strongest lines in lead tetramethyl have been omitted or indicated by an intensity of zero. The results obtained by Gopala Pai confirmed those of Venkateswaran (619) in so far as the work is duplicated. The usual C—H lines from $\Delta\bar{\nu}$ 2890 to 3000 are present, as well as lines near 1100. However, lines near $\Delta\bar{\nu}$ 1450 are absent in several of the compounds including the ethyl derivatives. For zinc dimethyl if $\Delta\bar{\nu}$ 488 and 505 are considered a doublet then the fundamental frequencies are $\Delta\bar{\nu}$ 144, 488 to 505, and 620. This yields a value of 1.6 × 10^5 dynes $cm.^{-1}$ for the Zn—C force constant.

If the fundamentals for mercury dimethyl are considered to be $\Delta\bar{\nu}$ 156, 515, and 700 the force constant is found to be 2.1 × 10^5 dynes $cm.^{-1}$. The spectrum of bismuth trimethyl is somewhat similar to that of arsenic trichloride, antimony trichloride, bismuth trichloride, and trimethylamine. Its fundamental frequencies are $\Delta\bar{\nu}$ 171, 460, and 1147; presumably it has a pyramid structure. The spectrum of the tetraalkyls resembles that of the tetrachlorides. The fundamental frequencies for tin tetramethyl are $\Delta\bar{\nu}$ 152, 262, 506, and 526, and for lead tetramethyl $\Delta\bar{\nu}$ 96, 165, 444, 462.

TABLE 36

The Raman spectra of some metallo derivatives

$\Delta\bar{\nu}$					
$Pb(CH_3)_4$	$Bi(CH_3)_3$	$Zn(CH_3)_2$	$Hg(CH_3)_2$	$Hg(C_2H_5)_2$	$Sn(CH_3)_4$
130(8)		144(2)	156(2)	140(1)	152(7)
	171(4)			212(2)	
		248(1)	255(0)	259(3)	262(4)
				329(0)	
460(5)	480(8)	488(2)		486(8)	
473(2)		505(8)	515(8)		506(8)
			565(1)	562(0)	526(5)
		620(4)		633(0)	
			700(3)		
	784(0)				
				958(1)	952(0)
				1008(3)	
				1055(2)	1046(0)
1155(2)	1147(2)	1159(6)			
1170(1)	1165(3)		1182(6)	1178(6)	1200(5)
	1230(1)		1258(1)		1262(0)
	1347(0)	1346(0)		1370(1)	
				1421(3)	
				1455(3)	
2291(0)			2879(1)	2857(1)	
2918(5)	2915(1)	2897(3)	2910(2)	2896(3)	2915(3)
2999(3)			2965(1)	2942(1)	2979(2)
3679(0)					
3755(0)					

It is concluded that the dialkyl metallo compounds may be treated as non-linear triatomic models of the type XY_2, that the trialkyls have a pyramidal structure, and that the tetraalkyls are represented by a regular tetrahedron.

W. The Raman spectra of deuterium compounds

Although hydrogen for the purpose of this discussion is considered with the inorganic compounds, it is of some interest to indicate the spectrum D_2 in comparison with it. For the transition in the zero vibrational level corresponding to Δj 0→2 according to Anderson and Yost, the Raman shift observed is $\Delta\bar{\nu}$ 179.6. For Δj 1→3 the Raman shift is $\Delta\bar{\nu}$ 298. In the first vibrational level where Δj corresponds to 2→2, the shift obtained is $\Delta\bar{\nu}$ 2989. The shifts for the corresponding changes in the rotational and vibrational quantum numbers for ordinary hydrogen are respectively $\Delta\bar{\nu}$ 354, 587, and 4144. In applying the simplest harmonic oscillator equation it is observed that

$$\frac{\Delta\bar{\nu}_{D_2}}{\Delta\bar{\nu}_{H_2}} = \frac{\sqrt{\bar{\mu}_{H_2}}}{\sqrt{\bar{\mu}_{D_2}}} = \frac{1}{\sqrt{2}}$$

or $\Delta\bar{\nu}_{D_2} = 2935$ for the calculated D_2 shift.

For water the strong O↔D oscillation according to Wood is $\Delta\bar{\nu}$ 2517. Rank, Larsen, and Bordner observed $\Delta\bar{\nu}$ 2666 and Ananthakrishnan $\Delta\bar{\nu}$ 2646, all of which indicate a mass effect without much change in force constant on comparing this shift with the $\Delta\bar{\nu}$ 3660 band in water.

Dadieu and Engler (149) have studied CD_4 and obtained $\Delta\bar{\nu}$ 2108 (8), 2141 (1), which are to be compared with $\Delta\bar{\nu}$ 2915 and $\Delta\bar{\nu}$ 3020 observed in CH_4. MacWood and Urey (416) found four vibrational lines in methane-d corresponding to $\Delta\bar{\nu}$ 1330, 2183, 2302, and 2920. Redlick and Pordes (539) and Wood and Rank (662) investigated chloroform-d. It is observed that the two lower shifts $\Delta\bar{\nu}$ 262 (10) and 366 (8) are identical with the equivalent shifts in chloroform. $\Delta\bar{\nu}$ 668 (8) and 761 (8) in chloroform appear as $\Delta\bar{\nu}$ 650 (8) and 738 (8) in $CDCl_3$. However, $\Delta\bar{\nu}$ 1215 (4) and 3019 (8) in chloroform are much more strongly altered by the isotope effect and yield $\Delta\bar{\nu}$ 908 and 2256. It is to be expected that where the chlorine is involved as an oscillator with respect to the carbon atom, a small increase in hydrogen mass will affect the spectra little, but where hydrogen is the origin of oscillation, whether of the bending or the linear type, the effect will be large, consequently the deuterium compounds will be of considerable value in correlating doubtful vibrations with the spectra. This is shown also in acetic acid-d_4. The shifts observed by Angus, Leckie, and Wilson are $\Delta\bar{\nu}$ 411, 580, 800, 1025, 1093, 1657, 2150, and 2218 as compared with $\Delta\bar{\nu}$ 447, 621, 895, 1360, 1430, 1666, 2942, and 3022 for CH_3COOH, which shows clearly what shifts are connected with the C—C, C═O, and C—H oscillations. The substitution of deuterium in oxdiazoles, furazans, and furans would aid considerably in the interpretation of their spectra.

The O↔D vibration in CH_3OD appears at $\Delta\bar{\nu}$ 2440, close to the expected value (539).

According to Trumpy (609) the strength of the C—D binding in the *cis*- and *trans*-dichloroethylene-d_2 and in tetrachloroethane-d_2 is slightly greater than in the corresponding hydrogen compounds. In tetrachloroethane the C—H ($\Delta\bar{\nu}$ 2984) becomes $\Delta\bar{\nu}$ 2240 for C—D and in dichloroethylene the C—H ($\Delta\bar{\nu}$ 3080) becomes $\Delta\bar{\nu}$ 2325 for C—D. Glockler and Davis (252) and Glockler and Morrell (256) have obtained $\Delta\bar{\nu}$ 1762 and 2700 for $DC{\equiv}CD$ as compared with $\Delta\bar{\nu}$ 1975 and 3374 in $HC{\equiv}CH$. In this case, the equation

$$\Delta\bar{\nu} = 4.125\sqrt{\frac{F}{}}$$

assuming a value for F of 15.05×10^5 dynes $cm.^{-1}$, calculated from ordinary acetylene linkage, leads to $\Delta\bar{\nu}$ 1901 as the expected $C{\equiv}C$ frequency, taking into consideration mass changes only. This does not agree with the observed result. Sutherland (583), Morino (455), and Glockler and Morrell (256) have made other calculations, based on somewhat different equations, that result in reasonable agreement.

Of the aromatic deuterium compounds C_6H_5D (18, 334), C_6HD_5 (334), and C_6D_6 (18, 334, 660) have alone been investigated. From C_6D_6 (660) are obtained $\Delta\bar{\nu}$ 581, 662, 873, 945, 1000, 1548, 2031, 2266, 2293, 2575, 3052 and 3108. $\Delta\bar{\nu}$ 1000 and 2031 are faint. A comparison of these shifts obtained with C_6H_6 (605, 849, 991, 1178, 1584, 1606, 2947, 3042, 3062, 3157, 3176, 3573, and 3627) shows that the shifts most affected are those greater than 2900 attributed to C—H, and $\Delta\bar{\nu}$ 1178 and 849. This would seem to settle beyond doubt that the last two frequencies involve hydrogen motions.

The possible types of motion giving rise to various frequencies are discussed by Angus and others (18).

While the deuterium compounds are of special interest in particular cases, their spectra are of no more importance, in general, than those of any other compounds.

V. VARIOUS APPLICATIONS OF THE RAMAN EFFECT

Up to this point the discussion of the Raman effect has been based primarily upon the intensity and magnitude of the Raman shifts and the fact that the Raman spectra are largely independent of the state of aggregation. It has been assumed that any variation from the normally expected Raman frequency was because of constitutional modification. In most cases these variations have been severely circumscribed. In this section will be discussed other causes of modified Raman spectra, such as the influence of solvents, hydrate formation, temperature, and electric fields.

A. Mixtures

Examples have already been given of polymerization and constitutional changes as depicted by Raman spectra. These were the cases of paraldehyde and formaldehyde. Before proceeding further in the discussion of other examples, it would be appropriate to point out the results of certain investigations with mixtures. Dadieu and Kohlrausch (170) investigated mixtures of benzene and chloroform, benzene and acetic acid, ethyl ether and hexachloroethane, methyl nitrite and methyl alcohol, and other mixtures of alcohols, esters, and acids in varying proportions. In all cases the final spectra obtained were the sum of the spectra of the individual components for those lines which were observed. In a few cases where one of the components is known to be associated into double molecules (such as the case of acetic acid), there is a slight but noticeable change in the spectrum of the mixture as compared with the spectra of the individual components.

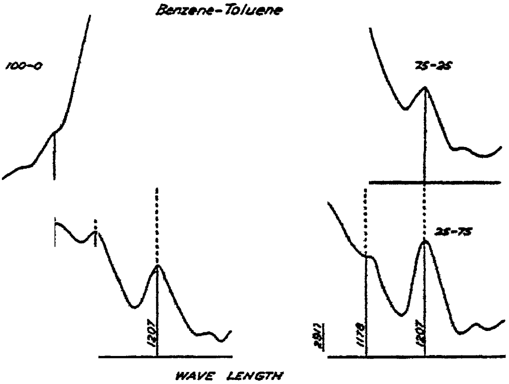


FIG. 29. The Raman spectra of benzene–toluene mixtures (after Crigler)

Krishnamurti (380) noted that a new faint line appears in 95 per cent acetic acid at $\Delta\bar{\nu}$ 1712 which is not present in the pure acid. The carbonyl shift in the pure acid is $\Delta\bar{\nu}$ 1667. The relative intensity of the $\Delta\bar{\nu}$ 1712 shift increases with dilution, until at 75 per cent concentration there remains only a broad line corresponding to this value. Mixtures of various acids, anhydrides, and alcohols have been studied by Parthasarathy (490). Whiting and Martin (645) examined mixtures of pyridine and acetic acid and of acetone and carbon disulfide. In every case the spectra of the pure substances appeared in solution. The abnormalities apparent in the vapor pressure and other physical properties of non-ideal solutions are not necessarily visibly reflected in the Raman spectra. Krishnamurti (379), on the other hand, so far as pyridine is concerned, observed appreciable changes in the position and intensity of some of the lines of pyridine on dilution with water. The principal lines affected were $\Delta\bar{\nu}$ 1029 and 1571. In methyl alcohol the line at $\Delta\bar{\nu}$ 1030 broadens in solution but becomes sharper at 50 per cent and has shifted to $\Delta\bar{\nu}$ 1018. It is suggested that these alterations indicate hydrate formations, particularly in view of the fact that the maximum change occurs at the proper hydrate concentration. Crigler (139, 141) has studied quantitatively mixtures of benzene and toluene in varying proportions. Twenty-five per cent changes in concentrations were easily perceptible, and 5 per cent changes possibly estimated. These results are shown in figure 29.

Lespieau, Bourguel, and Wakeman (406) have in a somewhat similar fashion determined the presence of unsaturateds in mixtures of cyclopropanes.

B. Solutions

The effect of water on the Raman spectra of nitric acid and sulfuric acid, and, conversely, the effect of inorganic compounds on the spectrum of water have been summarized by Hibben (311). Organic acids as well as inorganic acids also modify the water spectrum (535).

Hibben (310) has investigated compound formation between inorganic salts and organic alcohols. Zinc chloride in concentrated solution reduces the $\Delta\bar{\nu}$ 1034 shift in methyl alcohol by 22 wave numbers and increases $\Delta\bar{\nu}$ 2835 and 2944 by about the same amount; at the same time it diminishes the intensity at $\Delta\bar{\nu}$ 1450. Simultaneously there is a marked intensity change in the spectrum of zinc chloride. There is considerably less effect in ethyl alcohol than in methyl alcohol. Goubeau (270) has noted a similar effect in alcoholic solutions of lithium perchlorate. Brodskiĭ and Sack (108) and Sack and Brodskiĭ (549) observe no change in the spectra of benzene, methyl alcohol, ethyl alcohol, and carbon tetrachloride on dissolving arsenic trichloride in them, but there is a reduction of about 25 wave numbers in the lower frequency shifts of the arsenic trichloride. Voge (631) observes that lithium bromide will modify the shifts $\Delta\bar{\nu}$ 1034, 2835, and 2944 in methyl alcohol, first in the direction of slightly increased shifts with a 7 molal solution and subsequently in the direction of decreasing $\Delta\bar{\nu}$ 1034 and increasing further the last two shifts in a 24 molal solution.

The hydrolysis and dissociation of weak organic bases such as urea and hexamine have been shown by Krishnamurti (377) from the alteration in the Raman spectra of these compounds.

C. Association and polymerization

The supposed association of ethyl alcohol has been noted by an alteration in the shift $\Delta\bar{\nu}$ 623, according to Leitman and Ukhodin (403). Other evidence of association has been indicated by Meyer (436). Trumpy (606) has suggested a possible polymerization of formaldehyde in solution. More definite evidence of polymerization has been found by Signer and Weiler (559, 560). The spectrum of polystyrene is compared with that of ethylbenzene and styrene. The silica esters show modified spectra with increased polymerization. As has been previously mentioned, Venkateswaran and Bhagavantam (627) demonstrated the polymerization of acetaldehyde. Evidence of polymerization and depolymerization of inorganic compounds is plentiful.

D. Temperature

The effect of temperature on Raman spectra introduces no anomaly but some modification. As the number of molecules in the upper vibrational levels increases with increased temperature, there is a natural augmentation in the intensity of the anti-Stokes lines and other lines become more diffuse (236, 237). Bär (25) found a slight increase in intensity in some lines in diethyl ether at low temperature, but no discontinuity at $-105.4°$C., where there is an anomalous specific heat and density. Similarly Hertlein (308) observed no change in the spectrum of nitrobenzene just above the melting point, where there is a sharp change in dielectric constant. Epstein and Steiner (227) found a decrease of 1.7 wave numbers in benzene at $-20°$C. Sirkar (572) has noted modifications in some of the benzene lines at temperatures between 35° and 160°C. Experiments near the critical temperature by Placzek (510) indicate no alteration in the Raman spectra of the strong isobutyric acid lines, although this result is doubtful (672).

E. Electric and magnetic fields

Cotton (135) has noted that a strong magnetic field increases the intensities of $\Delta\bar{\nu}$ 1112, 1342, and 1587 in nitrobenzene. An electric field of 15,000 to 25,000 volts cm.$^{-1}$ causes an alteration in the depolarization factor of some lines in cyclohexane, benzene, and chlorobenzene (573).

F. Liquid rotational scattering

Bhagavantam (51, 53) and Bhagavantam and Rao (55) have discussed the question of "wings" accompanying Rayleigh scattering. In gases these have been attributed to unresolved lines of Raman scattering, the intensity distribution first increasing to a maximum and then decreasing with the distance from the Rayleigh line. These wings also exist in certain liquids, but it is only in liquid hydrogen that they have been completely resolved. In benzene the wings extend about 60 to 100 wave numbers. Bhagavantam (51) and Gross and Vuks (287) believe that the wings are attributable to internal oscillations in the liquid similar to those existing in solids, rather than to true rotational scattering. Mizushima and Morino (449, 450) and Mizushima, Morino, and Higasi (451, 452) have discussed the Raman effect and dipole moment in relation to free rotation. Meyer (438), Gross and Vuks (323), Rao (534), Sirkar (575, 576), Sirkar and Maiti (577), and Trumpy (607) have examined rotational scattering. There is still apparently some disagreement as to the explanation of the wings.

G. Specific heat and latent heat of fusion

If it is possible to identify Raman lines with definite modes of vibration in a molecule and to assign the correct number of degrees of freedom to each frequency, then, on the assumption that the vibrator in the molecule acts as an independent Einstein oscillator, it is possible to calculate the specific heat. In other words, since the Einstein expression gives the specific heat of a harmonic oscillator in terms of its frequency and temperature, the amount of heat a particular type of motion would absorb can be calculated by knowing its frequency and the number of degrees of freedom. The summation of these gives the specific heat of the molecule as a whole. This is the procedure Andrews (15) and Andrews and Southard (17) have used in calculating the specific heats of methyl alcohol, ethyl alcohol, benzene, bromobenzene, and other compounds with an average deviation of 5 per cent between 15° and 260°K.

With inorganic compounds Paramasivan has calculated the specific heats of compounds up to pentatomic molecules, using the Einstein specific heat functions and the Lindemann equation (311).

Phillips (503) has calculated the latent heat of fusion of some thirty-eight organic and inorganic substances from observed Raman shifts with reasonable agreement for the non-associated substances. The equation employed by him is

$$\lambda_\mu = \frac{mNhc}{JML_f} = \frac{m(2.845 \times 10^4)}{ML_f}$$

where m is an integer 1, 2. . . . , N is Avogadro's number, h is Planck's constant, c is the velocity of light, J is Joule's equivalent, ML_f is the molecular latent heat of fusion, and λ is the wave length, expressed in microns, in the infra-red corresponding to the Raman shift.

This may be expressed as:

$$\Delta\bar{\nu}(\text{cm.}^{-1}) = \frac{ML_f}{m} \times 0.351$$

This goes back to the fundamental assumption that $E = h\nu$ where E is the energy per molecule in the process involved. The extrapolation of this to the calculation of frequencies in chemical processes has been unsuccessfully attempted by Perrin. Phillips, on the other hand, proposes that since a change in vibrational states in the liquid or solid is possible, consequently the resultant energy change is equal to an integral part of the latent heat of fusion per molecule. There is no obvious explanation of these results, although the calculated latent heats agree with the observed values generally within ±4.5 per cent.

It is to be pointed out that

$$\frac{JML_f}{N} = H\bar{\nu}c = 1/2\ \bar{a}^2F$$

where $\frac{1}{2}\bar{a}F$ is the mean restoring force and $\bar{a}$ is the displacement during oscillation.

H. Intensities

The relative intensities of the Raman lines have been given in most cases. These are generally visual estimates of unknown accuracy. Several references will be cited here of more accurate determinations or cases where the determination was made with reference to the primary intensity of the Rayleigh scattering. These references are as follows: Dhar (204), Ellenberger (221), Haberl (290), Ray-Chaudhuri (537, 538), Rekveld (541), Sirkar (563), Werth (640, 641), and Weiler (634, 636). The most comprehensive theoretical treatment of intensities and polarization is that of Placzek (511).

VI. DEPOLARIZATION AND RAMAN SPECTRA

It is well known that general Rayleigh scattering is polarized, or in other words the ratio of the intensity of the horizontal light vibration in the scattered light i to the vertical vibration I (which is usually preponderant) approaches zero. In Raman spectra, if the type of vibration giving rise to the Raman line is unsymmetrical, the scattered radiation will not be completely polarized but will be depolarized to a greater or less degree depending on the character of the oscillation. Consequently the ratio of i/I augments and approaches approximately 6/7 as a limit, because complete depolarization can never be realized. The ratio i/I is expressed by rho (ρ), the depolarization factor, and it is in terms of this factor that depolarization measurements are generally reported.

In actual practice depolarization measurements are exceedingly difficult, since the experimental arrangement requires the complete elimination of parasitic light. The various methods employed and results obtained with inorganic substances have been summarized by Hibben (311). Placzek (510, 511) has discussed the theoretical aspects in complete detail.

The intrinsic importance of depolarization measurements can not be overemphasized. By them the types of motion giving rise to a Raman line in some cases can be determined irrespective of the magnitude of the Raman shift or its intensity. For example, the transverse oscillations of the C—H are strong but are not symmetrical. In consequence the depolarization factor is large. These shifts can thus be distinguished by this means from any —C═C— linkage of the furans which occur in the same neighborhood. Then again, in phosphorus trichloride and phosphorus tribromide the magnitudes of the Raman shifts are entirely different, but the relative depolarizations are nearly identical. Cabannes and Rousset (117) have determined the depolarization of a number of organic substances as well as inorganic ones. Simons (561) has likewise investigated and discussed the depolarization of organic compounds. His observations are given in table 37. Particular attention is called to the low depolarization in the neighborhood of 17 per cent ($\rho = 0.17$) for the symmetrical oscillations. Venkateswaran (625) has recently investigated the polarization of a variety of compounds. He observes in methyl mercaptan that the lowest depolarization factor is 0.3 (30 per cent) for $\Delta\bar{\nu}$ 2573 corresponding to the S—H linkage, $\Delta\bar{\nu}$ 2932 for the C—H linkage, $\Delta\bar{\nu}$ 704 for the C—S linkage, respectively. Other than $\Delta\bar{\nu}$ 1059 the remainder of the lines have depolarization values varying from 0.4 to 0.9. In carbon tetrachloride $\Delta\bar{\nu}$ 459 has a value of 0.04, as compared with 0.3 for $\Delta\bar{\nu}$ 1535 and 0.8 for the remainder of the lines. In pentane the two lowest values of ρ are found for $\Delta\bar{\nu}$ 839 and 2876, clearly indicating the most symmetrical vibrations. It is quite evident that $\Delta\bar{\nu}$ 1385 in pyrrole is a transverse oscillation, as its depolarization is 0.5. Generally the lines of the aliphatic compounds are more polarized than those of the aromatic. When a frequency becomes a doublet, the resulting pair of lines will usually have the same degree of polarization as the original. When a Raman line is excessively broad, as in the O—H shift, the depolarization will be marked, even though the oscillation corresponds to a supposedly symmetrical vibration.

Some other workers who have contributed to this field of Raman spectra are as follows: Bhagavantam (35, 41, 48, 49), Bhagavantam and Venkateswaran (58), Cabannes (112, 113, 114), Cabannes and Rousset (116), Daure (199), Hanle (291, 292, 293, 294), Kastler (329), Lindemann, Keeley, and Hall (412), Menzies (434), Mesnage (435), Ornstein and Stoutenbeek (482), Paulsen (494), Placzek (510, 511), Rousset (546, 547), Saha and Bhargava (550), Sirkar (573, 574), Trumpy (606, 607, 608, 610), Venkateswaran (624, 625), and Weiler (636).

It is with a feeling of regret—not unmixed with relief—that practically

TABLE 37

The degree of depolarization of some organic compounds

SUBSTANCE	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ
C_6H_6																602	3	0.86	844	1		991	10	0.7
C_6H_5Cl	195	3	0.87	293	1	0.86	415	2	0.32	484	½					607	1	0.89	689	2	0.13	999	4	0.6
$C_6H_5CH_3$	211	4	0.91										517	2	0.34	619	2	0.85	781	4	0.10	1002	4	0.7
$C_6H_5OCH_3$	(194)	2	0.88	258	2	0.85				436	3 br.	(0.37)	529	½		607	2	0.87	778	4	0.7	991	5	0.7
C_6H_5CHO	214–280	2	(0.87)							438	3	0.33				612 (642)	3 1	0.89	824	3	0.7	1000	5	0.7
C_6H_5CN	170	4 br.	0.85				379	0	0.36	(460)	(½)		545	1		619	1	0.84	754	2 br.	0.15	998	5	0.4
$C_6H_5COCH_3$	161	4	0.87				388	1	0.36							613	3	0.82	731 946	3 1	0.22	999	5	0.4
C_6H_5COCl	161	3 br.	0.84				314	3	0.24	412	1	0.39	505	3	0.19	615	3	0.92	670 771	3 ½	0.15	1003	6	0.7
$C_6H_4(CH_3)_2$	218	3	0.89	(307)	½	(0.90)				528	3 br.	0.25							724	4 br.	0.8	819	1 br.	0.15
$C_6H_4(CH_3)_2$ mixture)	228	3	0.88	(312)	1					535	3 doub.	0.32	580	2	0.33				729	5 br.	0.7	825	3 br.	0.8
CF COOH							440	3	0.59				614	5	0.89				889	6	0.16			
$CH_3COOC_2H_5$	381	4	0.37													637	4	0.23	852	3	0.17	938	0 br.	
$C_2H_5COOC_2H_5$ ...	(367)	2	0.34										(611)	0	0.57	778	00	0.43	855	2	0.15			
$C_3H_7COOC_2H_5$ ...	323	1	0.42	(385)	0								604	0 br.					871	1 v. br.	0.23			
CH_3OH																								
C_2H_5OH							431	1	0.55										880	5	0.31			
CH_3COCH_3				391	2	0.87	491	1		526	3	0.70							784	10	0.20	902	00	
$CH_3COC_2H_5$				396	½	0.87				579	½	0.73							757	2	0.19	812	½	
$C_2H_5OC_2H_5$							436	5	0.48	510	1								840	5	0.29			
C_3H_7Cl.	359	3	0.55										644	4	0.15	721	2 br.	0.30	782	2	0.16	(845) (890)	2 2	

SUBSTANCE	$\Delta\tilde{\nu}$	i	ρ	$\Delta\tilde{\nu}$	i	ρ	$\Delta\tilde{\nu}$	i	ρ	$\Delta\tilde{\nu}$	i	ρ	$\Delta\tilde{\nu}$	i	ρ	$\Delta\tilde{\nu}$	i	ρ	$\Delta\tilde{\nu}$	i	ρ
C_6H_6							1178	3	0.89										1362	½ br.	
C_6H_5Cl	1019	1	0.19	1070	1 br.	0.10	1152	1 br.	0.88										(1381)	½ br.	
$C_6H_5CH_3$	1027	1	0.27				1154	1	0.88				1207	3	0.25				1376	1 br.	0.42
$C_6H_5OCH_3$	1023	2 br.	0.9	(1060)	2	0.11	1150	1	(0.94)	1174	3 br.	0.34	1240	3 br.	0.25	(1294)	1 br.	0.31			
C_6H_5CHO							1159	3	(0.63)				1200	4	0.35				1388	½	0.36
C_6H_5CN							1175	2					1190	3	0.24						
$C_6H_5COCH_3$	1025	3	0.24	1074	4	0.16	1155	1	(0.72)							1263	3	0.17			
C_6H_5COCl				1028	2	0.13	1168	3 br.	(0.65)				1206	3 br.	0.30						
$C_6H_4(CH_3)_2$	1004	4	0.5													(1342)	2	(0.35)	1374	2	0.37
$C_6H_4(CH_3)_2$ mixture	1007	4	0.3	1044	2	0.30							1251	3	0.43				1373	4	0.38
CH_3COOH													1280	1 br.		1368	4 br.	0.21	1432	4 br.	0.85
$CH_3COOC_2H_5$	1005	0 br.	0.62	1044	0 br.	0.60	1100	2	0.60										1442	3 br.	0.88
$C_2H_5COOC_2H_5$	989	0 br.	0.54	(1092)	0	0.56													1450	2 br.	0.86
$C_3H_7COOC_2H_5$				1034	1 br.	0.66	(1106)	½	(0.71)				(1277)	½ v. br.					1447	3	0.89
CH_3OH				1035	4	0.64													1454	3 v. br.	0.91
C_2H_5OH				1050	3	0.59	1098	1					1276	1					1457	4 br.	0.90
CH_3COCH_3	923	1 br.		1069	3	0.64				1192	3	0.88	1227	5	0.88	(1340)	½	0.23	1430	5 br.	0.90
$CH_3COC_2H_5$				(1069)	0	0.59										1337	2 br.	0.16	1414	2 br.	0.89
																			1445	2 br.	0.87
$C_2H_5OC_2H_5$	928	3	0.61	1037	3	0.56				1147	3		1276	4 br.	0.90				1454	4 br.	0.89
C_3H_7Cl	1026	3	0.53																1442	4 v. br.	0.85
		C—C			C—O															C—H	

TABLE '—C

SUBSTANCE	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ	$\Delta\bar{\nu}$	i	ρ
C_6H_6				1586	3 br.	0.89													2945	4 br.	0.89	3056	8 br.	0.34
				1603	1	0.87																		
C_6H_5Cl				1576	2 br.	0.87																3059	5 br.	0.32
$C_6H_5CH_3$				1599	2 br.	0.92										2917	0 br.	0.29	2984	0	0.74	3048	5 br.	0.34
$C_6H_5OCH_3$	1454	1 br.	0.87	1594	4	0.92													2949	3 br.	0.80	3062	5 br.	0.33
C_6H_5CHO	(1452)	0	0.91	1594	7	0.88	1696	7	0.42										(2922)	3 br.		3057	3 br.	0.35
C_6H_5CN				1595	4	0.88				2227	5	0.23										3063	4 br.	0.30
$C_6H_5COCH_3$	1483	½	0.87	1597	6	0.86	1679	5	0.32							2923	4 br.	0.21				3063	4 br.	0.35
C_6H_5COCl				1592	6	0.84	1744	4	0.34													3067	4 br.	0.33
$C_6H_4(CH_3)_2$	1443	1 br.	0.91	(1597)	2	0.85							2849	1	0.6	2917	4	0.27				3042	4 br.	0.34
$C_6H_4(CH_3)_2$ mixture)	1447	4	0.88	(1597)	4	0.85							(2863)	3	0.8	2917	5 br.	0.26				3048	4 br.	0.35
		C—H						C=O			C≡N			C—H			C—H			C—H			C—H	
CH_3COOH	(1669)	4 br.	0.37				2940	10 br.	0.4															
$CH_3COOC_2H_5$	(1724)	2	0.42				2921	5	0.19	2960	3	0.87												
$C_2H_5COOC_2H_5$	(1719)	1	0.36				2936	3 br.	0.20	2977	3	0.86												
$C_3H_7COOC_2H_5$	(1728)	1	0.38	2868	3	0.4	2932	3 v. br.	0.19															
CH_3OH				2832	8	0.7	2941	7	0.22				3388±85	2 br.	0.89									
C_2H_5OH				2873	5 br.	0.14	2926	8 br.	0.23	2974	5	0.87												
CH_3COCH_3	1714	5	0.38				2922	10	0.22															
$CH_3COC_2H_5$	(1710)	2	0.38				2913	4 br.	0.15	2973	3 br.	0.89												
$C_2H_5OC_2H_5$				2866	10 br.	(0.30)	2932	10	0.20	2980	8 br.	0.89												
C_3H_7Cl				2870	5	0.8	2938	6 v. br.	0.25															
		C=O			C—H			C—H			C—H			O—H										

all reference in this discussion to infra-red absorption has been omitted. It might be considered a fourth parameter necessary in the complete treatment of Raman spectra, but is a separate field of investigation. The contributions of Wulf and Liddel and many others to the elucidation of organic structure by this means lead to conclusions reasonably compatible with the results obtainable from Raman spectra investigations. On the other hand, there are occasions involving the asymmetrical oscillations of light atoms when the infra-red is the more valuable approach. This has been omitted from consideration for reasons which have already been given.

VII. CONCLUSION

It has been the purpose of this review to discuss, at least in principle, all the developments in the Raman effect as applied to organic chemistry since its discovery in 1928. The spectra obtained from every type of organic compound and type of linkage have been given in some detail. The application of the Raman effect in the delineation of the structure of organic compounds has been indicated. It can not be too strongly emphasized that these same principles apply not only to organic chemistry but to inorganic chemistry as well. The utility of this method in providing information regarding other physical properties of compounds has been considered. An index and bibliography have been included in which are recorded most of the citations with reference to organic compounds so far published, in the hope that these will be of value to those who wish to investigate in more detail the spectrum of any type of compound.

The Raman effect has reached a stage of more quantitative investigation. Its development may be somewhat slower in the future than in the past. Its contributions, nevertheless, to a greater understanding of the constitution of matter regardless of the stage of aggregation have been by no means negligible.

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PART I. ALIPHATIC COMPOUNDS[1]

A. SATURATED COMPOUNDS

I. Hydrocarbons

(1)	CD_4	CD_4 methane-d$_4$ (149)
(2)	$C_5H_{11}D$	$(CH_3)_3CCH_2D$ tetramethylmethane-d (533)
(3)	C	C diamond (34, 37, 40, 43, 54, 468, 527, 528, 545)
(4)	CH_4	CH_4 methane (47, 49, 50, 59, 194, 195, 196, 197, 205, 344, 411, 416, 424, 425, 467, 613, 650)
(5)	C_2H_6	C_2H_6 ethane (47, 54, 69, 194, 196, 197, 345, 349)
(6)	C_3H_8	C_3H_8 propane (47, 69, 194, 197, 345, 349)
(7)	C_4H_{10}	C_4H_{10} butane (47, 345, 349, 462)
(8)	C_4H_{10}	$(CH_3)_3CH$ isobutane (47, 345, 349)
(9)	C_5H_{12}	C_5H_{12} pentane (41, 73, 158, 242, 349, 523, 635)
(10)	C_5H_{12}	$(CH_3)_2CHCH_2CH_3$ isopentane (349, 373)
(11)	C_5H_{12}	$C(CH_3)_4$ tetramethylmethane (2,2-dimethylpropane) (344, 345, 349, 532, 533)
(12)	C_6H_{14}	C_6H_{14} hexane (6, 7, 9, 28, 259, 349, 359, 452, 480, 498, 510, 513)
(13)	C_6H_{14}	$(CH_3)_2CH(CH_2)_2CH_3$ isohexane (9)
(14)	C_6H_{14}	$(C_2H_5)_2CHCH_3$ methyldiethylmethane (3-methylpentane) (9)
(15)	C_6H_{14}	$(CH_3)_3CC_2H_5$ trimethylethylmethane (2,2-dimethylbutane) (9)
(16)	C_6H_{14}	$(CH_3)_2CHCH(CH_3)_2$ diisopropyl (2,3-dimethylbutane) (7, 9)
(17)	C_7H_{16}	C_7H_{16} heptane (73, 133, 242, 349, 569)
(18)	C_8H_{18}	C_8H_{18} octane (73, 133, 242, 349, 381)
(19)	C_8H_{18}	$(CH_3)_2CH(CH_2)_2CH(CH_3)_2$ 2,5-dimethylhexane (460)
(20)	C_8H_{18}	$C_2H_5CH(CH_3)CH(CH_3)C_2H_5$ 3,4-dimethylhexane (460)
(21)	C_8H_{18}	$CH_3C(CH_3)_2CH_2CH(CH_3)_2$ 2,2,4-trimethylpentane (533)
(22)	C_9H_{20}	C_9H_{20} nonane (6, 349)
(23)	C_9H_{20}	$(CH_3)_3CCH_2C(CH_3)_3$ 2,2,4,4-tetramethylpentane (533)

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[1] In this index are listed the empirical formula, the structural formula, the name, and the reference numbers for most of the organic compounds so far investigated. The order of arrangement in each group of compounds is approximately the same as used in *Chemical Abstracts* with the exception of the deuterium compounds, which are listed separately. Each compound is preceded by a number, which is its "formula number."

Such compounds as the nitro and cyano derivatives and the oximes are considered as saturated compounds unless they possess an ethylenic linkage. When an author publishes the same article in more than one journal (note, for example, many of the publications of Kohlrausch and his associates) both references are given in the bibliography, but both are not always cited in the formula index.

(24) $C_{10}H_{22}$	$C_{10}H_{22}$	decane (6, 73, 349)
(25) $C_{11}H_{24}$	$C_{11}H_{24}$	undecane (6, 349)
(26) $C_{12}H_{26}$	$C_{12}H_{26}$	dodecane (6, 349)
(27)		gasoline (8, 312)
(28)		oil (312)

II. Halogen derivatives of hydrocarbons

a. Fluorine derivatives

(29) CH_3F	CH_3F	methyl fluoride (1)

b. Chlorine derivatives

(30) $CDCl_3$	$CDCl_3$	chloroform-d (539, 662)
(31) $C_2D_2Cl_4$	$C_2D_2Cl_4$	tetrachloroethane-d_2 (609)
(32) CCl_4	CCl_4	carbon tetrachloride (24, 27, 34, 35, 36, 48, 57, 58, 108, 109, 112, 113, 117, 119, 120, 121, 122, 143, 157, 158, 170, 192, 193, 201, 221, 229, 236, 242, 291, 292, 293, 317, 344, 382, 390, 391, 392, 393, 394, 397, 412, 418, 433, 434, 435, 467, 482, 483, 512, 519, 525, 526, 534, 541, 543, 546, 552, 561, 563, 566, 567, 604, 625, 653, 654, 655)
(33) $CHCl_3$	$CHCl_3$	chloroform (27, 34, 35, 57, 113, 117, 129, 143, 162, 166, 170, 201, 242, 291, 292, 293, 304, 305, 394, 432, 433, 519, 561, 612, 625, 633, 654, 664)
(34) CH_2Cl_2	CH_2Cl_2	methylene chloride (57, 117, 162, 166, 169, 172, 400, 482, 519, 607, 608, 666)
(35) CH_3Cl	CH_3Cl	methyl chloride (1, 21, 117, 168, 169, 171, 172, 625, 642)
(36) C_2Cl_6	CCl_3CCl_3	hexachloroethane (57, 162, 166, 170, 376)
(37) C_2HCl_5	$CHCl_2CCl_3$	pentachloroethane (72, 495, 496, 595)
(38) $C_2H_2Cl_4$	$CHCl_2CHCl_2$	1,1,2,2-tetrachloroethane (68, 129, 162, 166, 221, 294, 435, 518, 519, 561, 595, 609, 610)
(39) $C_2H_3Cl_3$	$C_2H_2Cl_3$	trichloroethane (294, 561)
(40) $C_2H_3Cl_3$	CH_3CCl_3	1,1,1-trichloroethane (324, 350, 351)
(41) $C_2H_3Cl_3$	$CH_2ClCHCl_2$	1,1,2-trichloroethane (324, 350, 351)
(42) $C_2H_4Cl_2$	CH_3CHCl_2	1,1-dichloroethane (129, 337, 350, 351, 449, 450, 495, 496)
(43) $C_2H_4Cl_2$	CH_2ClCH_2Cl	1,2-dichloroethane (57, 72, 126, 129, 162, 166, 320, 337, 449, 450, 451, 452, 495, 496, 606, 610)
(44) C_2H_5Cl	C_2H_5Cl	ethyl chloride (129, 162, 166, 174, 177, 297, 578, 642)
(45) $C_3H_6Cl_2$	$CH_3CH_2CHCl_2$	1,1-dichloropropane (350, 351, 495, 496)
(46) $C_3H_6Cl_2$	$CH_3CHClCH_2Cl$	1,2-dichloropropane (495, 496)
(47) $C_3H_6Cl_2$	$CH_2ClCH_2CH_2Cl$	1,3-dichloropropane (495, 496)
(48) $C_3H_6Cl_2$	$CH_3CCl_2CH_3$	2,2-dichloropropane (350, 351, 495, 496)
(49) C_3H_7Cl	C_3H_7Cl	propyl chloride (57, 162, 166, 297, 495, 496, 561, 578, 642)
(50) C_3H_7Cl	$(CH_3)_2CHCl$	isopropyl chloride (2-chloropropane) (57, 185, 189, 297, 495, 496, 642)
(51) $C_4H_8Cl_2$	$CH_3CH_2CH_2CHCl_2$	1,1-dichlorobutane (350, 351)

(52) $C_4H_8Cl_2$	$(CH_3)_2CHCHCl_2$ dichloroisobutane (1,1-dichloro-2-methylbutane) (350, 351)
(53) C_4H_9Cl	C_4H_9Cl butyl chloride (174, 177, 297)
(54) C_4H_9Cl	$(CH_3)_2CHCH_2Cl$ isobutyl chloride (1-chloro-2-methylpropane) (57, 297, 373)
(55) C_4H_9Cl	$C_2H_5CHClCH_3$ *sec*-butyl chloride (2-chlorobutane) (186, 190, 297)
(56) C_4H_9Cl	$(CH_3)_3CCl$ *tert*-butyl chloride (2-chloro-2-methylpropane) (162, 166, 185, 189, 297)
(57) $C_5H_{10}Cl_2$	$CH_3(CH_2)_3CHCl_2$ 1,1-dichloropentane (350, 351)
(58) $C_5H_{10}Cl_2$	$(CH_3)_2CHCH_2CHCl_2$ dichloroisopentane (1,1-dichloro-3-methylbutane) (350, 351)
(59) $C_5H_{11}Cl$	$C_5H_{11}Cl$ amyl chloride (186, 190, 297, 532)
(60) $C_5H_{11}Cl$	$(CH_3)_2CH(CH_2)_2Cl$ isoamyl chloride (1-chloro-3-methylbutane) (186, 190, 297)
(61) $C_5H_{11}Cl$	$C_2H_5CH(CH_3)CH_2Cl$ 1-chloro-2-methylbutane (350, 351)
(62) $C_5H_{11}Cl$	$(CH_3)_2C(Cl)C_2H_5$ 2-chloro-2-methylbutane (185, 189, 297, 456)
(63) $C_5H_{11}Cl$	$CH_3(CH_2)_2CHClCH_3$ 2-chloropentane (350, 351)
(64) $C_5H_{11}Cl$	$C_2H_5CHClC_2H_5$ 3-chloropentane (350, 351)
(65) $C_5H_{11}Cl$	$(CH_3)_3CCH_2Cl$ 1-chloro-2,2-dimethylpropane (533)
(66) $C_6H_{13}Cl$	$C_6H_{13}Cl$ hexyl chloride (346, 347)
(67) $C_7H_{15}Cl$	$C_7H_{15}Cl$ heptyl chloride (346, 347, 349)
(68) $C_8H_{17}Cl$	$C_8H_{17}Cl$ octyl chloride (346, 347)
(69) $C_9H_{19}Cl$	$C_9H_{19}Cl$ nonyl chloride (346, 347)
(70) $C_{10}H_{21}Cl$	$C_{10}H_{21}Cl$ decyl chloride (346, 347)

c. Bromine derivatives

(71) CBr_4	CBr_4 carbon tetrabromide (174, 177, 344, 397, 586)
(72) $CHBr_3$	$CHBr_3$ bromoform (34, 35, 57, 117, 162, 166, 172, 201, 242, 625)
(73) CH_2Br_2	CH_2Br_2 methylene bromide (117, 169, 172, 174, 177, 258, 400, 608)
(74) CH_3Br	CH_3Br methyl bromide (1, 21, 117, 129, 168, 169, 171, 172, 625)
(75) C_2Br_6	CBr_3CBr_3 hexabromoethane (258)
(76) $C_2H_2Br_4$	$C_2H_2Br_4$ tetrabromoethane (129, 162, 166)
(77) $C_2H_2Br_4$	$CHBr_2CHBr_2$ 1,1,2,2-tetrabromoethane (258)
(78) $C_2H_4Br_2$	CH_3CHBr_2 1,1-dibromoethane (129, 258, 450, 451)
(79) $C_2H_4Br_2$	CH_2BrCH_2Br 1,2-dibromoethane (57, 126, 129, 162, 166, 449, 450, 452, 610)
(80) C_2H_5Br	C_2H_5Br ethyl bromide (57, 129, 162, 166, 578)
(81) $C_3H_5Br_3$	$CH_2BrCHBrCH_2Br$ tribromohydrin (1,2,3-tribromopropane) (371)
(82) C_3H_7Br	C_3H_7Br propyl bromide (57, 162, 166, 295, 578)
(83) C_3H_7Br	$(CH_3)_2CHBr$ isopropyl bromide (2-bromopropane) (185, 189, 295)
(84) $C_3H_6Br_2$	$CH_2BrCHBrCH_3$ 1,2-dibromopropane (258)
(85) $C_3H_6Br_2$	$CH_2BrCH_2CH_2Br$ 1,3-dibromopropane (174, 177)

(86)	C_4H_9Br	C_4H_9Br	butyl bromide (140, 163, 167, 295, 661)
(87)	C_4H_9Br	$(CH_3)_2CHCH_2Br$	isobutyl bromide (1-bromo-2-methylpropane) (57, 295, 373)
(88)	C_4H_9Br	$CH_3CH_2CHBrCH_3$	*sec*-butyl bromide (2-bromobutane) (186, 190, 295)
(89)	C_4H_9Br	$(CH_3)_3CBr$	*tert*-butyl bromide (2-bromo-2-methylpropane) (185, 189, 295)
(90)	$C_5H_{11}Br$	$C_5H_{11}Br$	amyl bromide (186, 190, 295)
(91)	$C_5H_{11}Br$	$(CH_3)_2CHCH_2CH_2Br$	isoamyl bromide (1-bromo-3-methylbutane) (186, 190, 295)
(92)	$C_5H_{11}Br$	$(CH_3)_2C(Br)C_2H_5$	2-bromo-2-methylbutane (185, 189)
(93)	$C_6H_{13}Br$	$C_6H_{13}Br$	hexyl bromide (140)
(94)	$C_7H_{15}Br$	$C_7H_{15}Br$	heptyl bromide (349)

d. Iodine derivatives

(95)	CH_2I_2	CH_2I_2	methylene iodide (169, 172, 400)
(96)	CH_3I	CH_3I	methyl iodide (1, 21, 117, 129, 168, 171, 174, 177, 263, 625)
(97)	$C_2H_4I_2$	CH_2ICH_2I	1,2-diiodoethane (126)
(98)	C_2H_5I	C_2H_5I	ethyl iodide (129, 168, 171, 174, 177, 264)
(99)	C_3H_7I	C_3H_7I	propyl iodide (174, 177, 264)
(100)	C_3H_7I	$(CH_3)_2CHI$	isopropyl iodide (2-iodopropane) (185, 189)
(101)	C_4H_9I	C_4H_9I	butyl iodide (174, 177)
(102)	C_4H_9I	$(CH_3)_2CHCH_2I$	isobutyl iodide (1-iodo-2-methylpropane) (264, 373)
(103)	C_4H_9I	$C_2H_5CHICH_3$	*sec*-butyl iodide (2-iodobutane) (186, 190)
(104)	C_4H_9I	$(CH_3)_3CI$	*tert*-butyl iodide (2-iodo-2-methylpropane) (185, 189)
(105)	$C_5H_{11}I$	$C_5H_{11}I$	amyl iodide (186, 190)
(106)	$C_5H_{11}I$	$(CH_3)_2CHCH_2CH_2I$	isoamyl iodide (1-iodo-3-methylbutane) (186, 190)
(107)	$C_5H_{11}I$	$C_2H_5C(CH_3)_2I$	*tert*-amyl iodide (2-iodo-2-methylbutane) (373)
(108)	$C_6H_{13}I$	$C_6H_{13}I$	hexyl iodide (350, 351)

e. Mixed halogen derivatives

(109)	CCl_2F_2	CCl_2F_2	dichlorodifluoromethane (107)
(110)	CCl_3Br	$CBrCl_3$	trichlorobromomethane (655)
(111)	$CHBrCl_2$	$CHBrCl_2$	dichlorobromomethane (79, 350, 351)
(112)	$CHCl_2F$	$CHCl_2F$	dichlorofluoromethane (107)

III. Alcohols

a. Monohydric alcohols

(113)	CDH_3O	CH_3OD	methyl alcohol-d (539)
(114)	CH_4O	CH_3OH	methyl alcohol (28, 108, 168, 170, 171, 194, 242, 248, 270, 291, 310, 330, 379, 427, 436, 452, 510, 513, 523, 539, 541, 542, 549, 561, 606, 625, 626, 629, 631, 645, 654, 661)

(115)	C_2H_5ClO	CH_2ClCH_2OH	β-chloroethyl alcohol (320, 428)
(116)	C_2H_6O	C_2H_5OH	ethyl alcohol (31, 63, 64, 108, 129, 162, 166, 168, 171, 192, 194, 242, 270, 291, 310, 323, 427, 475, 490, 546, 549, 561, 568, 597, 606, 626, 629, 654, 661, 666)
(117)	C_3H_8O	C_3H_7OH	propyl alcohol (1-propanol) (156, 194, 242, 427, 602, 606, 626, 661)
(118)	C_3H_8O	$CH_3CHOHCH_3$	isopropyl alcohol (2-propanol) (185, 189, 194, 242, 427, 602)
(119)	$C_4H_{10}O$	C_4H_9OH	butyl alcohol (1-butanol) (156, 350, 351, 427, 471, 602, 606, 626, 661)
(120)	$C_4H_{10}O$	$(CH_3)_2CHCH_2OH$	isobutyl alcohol (2-methyl-1-propanol) (242, 602, 626)
(121)	$C_4H_{10}O$	$C_2H_5CHOHCH_3$	*sec*-butyl alcohol (2-butanol) (373, 471, 602)
(122)	$C_4H_{10}O$	$(CH_3)_3COH$	*tert*-butyl alcohol (2-methyl-2-propanol) (185, 189, 427, 471, 602, 626)
(123)	$C_5H_{12}O$	$C_5H_{11}OH$	amyl alcohol (1-pentanol) (31, 186, 190, 291, 471, 661)
(124)	$C_5H_{12}O$	$(CH_3)_2CHCH_2CH_2OH$	isoamyl alcohol (3-methyl-1-pentanol) (31, 186, 190, 242, 291, 471, 629)
(125)	$C_5H_{12}O$	$C_3H_7CHOHCH_3$	*sec*-amyl alcohol (2-pentanol) (346, 347, 471)
(126)	$C_5H_{12}O$	$(CH_3)_2COHC_2H_5$	*tert*-amyl alcohol (2-methyl-2-butanol) (185, 189, 346, 347, 471)
(127)	$C_5H_{12}O$	$(C_2H_5)_2CHOH$	diethylcarbinol (3-pentanol) (346, 347, 471, 533)
(128)	$C_5H_{12}O$	$C_2H_5CH(CH_3)CH_2OH$	*sec*-butylcarbinol (2-methyl-1-butanol) (288, 346, 347)
(129)	$C_5H_{12}O$	$(CH_3)_3CCH_2OH$	*tert*-butylcarbinol (2,2-dimethyl-1-propanol) (346, 347, 471)
(130)	$C_5H_{12}O$	$(CH_3)_2CHCH(CH_3)OH$	methylisopropylcarbinol (3-methyl-2-butanol) (346, 347)
(131)	$C_6H_{14}O$	$(C_2H_5)_2(CH_3)COH$	diethylmethylcarbinol (3-methyl-3-pentanol) (551)
(132)	$C_6H_{14}O$	$C_6H_{13}OH$	1-hexanol (31, 661)
(133)	$C_7H_{16}O$	$C_7H_{15}OH$	1-heptanol (31, 661)
(134)	$C_8H_{18}O$	$C_7H_{15}CH_2OH$	1-octanol (31, 133, 471, 661)
(135)	$C_8H_{18}O$	$C_6H_{13}CHOHCH_3$	2-octanol (133, 471)
(136)	$C_8H_{18}O$	$C_5H_{11}CHOHC_2H_5$	3-octanol (133)
(137)	$C_8H_{18}O$	$C_4H_9CHOHC_3H_7$	4-octanol (133)
(138)	$C_8H_{18}O$	$(CH_3)_2CH(CH_2)_2C(CH_3)OHCH_3$	2,5-dimethyl-2-hexanol (10)
(139)	$C_8H_{18}O$	$(CH_3)_2CHCH_2C(CH_3)OHC_2H_5$	3,5-dimethyl-3-hexanol (10)
(140)	$C_8H_{18}O$	$C_5H_{11}C(CH_3)OHCH_2$	2-methyl-2-heptanol (133)
(141)	$C_8H_{18}O$	$C_4H_9C(CH_3)OHC_2H_5$	3-methyl-3-heptanol (133)
(142)	$C_8H_{18}O$	$C_3H_7C(CH_3)OHC_3H_7$	4-methyl-4-heptanol (133)
(143)	$C_8H_{18}O$	$C_5H_{11}CH(CH_3)CH_2OH$	2-methyl-1-heptanol (133)
(144)	$C_8H_{18}O$	$C_3H_7CHOHCH_2CH(CH_3)CH_3$	2-methyl-4-heptanol (133)
(145)	$C_8H_{18}O$	$C_4H_9CH(CH_3)CHOHCH_3$	3-methyl-2-heptanol (133)

(146) $C_8H_{18}O$ $C_3H_7CH(CH_3)CH_2CH_2CH_2OH$ 4-methyl-1-heptanol (133)

(147) $C_8H_{18}O$ $C_3H_7CH(CH_3)CH_2CHOHCH_3$ 4-methyl-2-heptanol (133)

(148) $C_8H_{18}O$ $C_3H_7CH(CH_3)CHOHC_2H_5$ 4-methyl-3-heptanol (133)

(149) $C_8H_{18}O$ $C_2H_5CH(CH_3)(CH_2)_3CH_2OH$ 5-methyl-1-heptanol (133)

(150) $C_8H_{18}O$ $C_2H_5CH(CH_3)(CH_2)_2CHOHCH_3$ 5-methyl-2-heptanol (133)

(151) $C_8H_{18}O$ $C_2H_5CH(CH_3)CH_2CHOHC_2H_5$ 5-methyl-3-heptanol (133)

(152) $C_8H_{18}O$ $CH_3CH(CH_3)(CH_2)_4CH_2OH$ 6-methyl-1-heptanol (133)

(153) $C_8H_{18}O$ $CH_3CH(CH_3)(CH_2)_3CHOHCH_3$ 6-methyl-2-heptanol (133)

(154) $C_8H_{18}O$ $CH_3CH(CH_3)(CH_2)_2CHOHC_2H_5$ 6-methyl-3-heptanol (133)

(155) $C_9H_{20}O$ $(CH_3)_2CHCH_2CH(CH_3)CHOHC_2H_5$ 4,6-dimethyl-3-heptanol (10)

(156) $C_9H_{20}O$ $(CH_3)_2CH(CH_2)_2C(CH_3)OHC_2H_5$ 3,6-dimethyl-3-heptanol (10)

(157) $C_9H_{20}O$ $(CH_3)_2CHCH_2C(CH_3)OHCH(CH_3)_2$ 2,3,5-trimethyl-3-hexanol (10)

(158) $C_9H_{20}O$ $C_9H_{19}OH$ nonyl alcohol (1-nonanol) (31, 661)

(159) $C_{10}H_{22}O$ $C_{10}H_{21}OH$ decyl alcohol (1-decanol) (661)

(160) $C_{10}H_{22}O$ $(CH_3)_2CHCH_2C(CH_3)OHCH_2CH(CH_3)_2$ 2,4,6-trimethyl-4-heptanol (10)

(161) $C_{10}H_{22}O$ $C_4H_9C(CH_3)OHCH_2CH(CH_3)_2$ 2,4-dimethyl-4-octanol (10)

(162) $C_{11}H_{24}O$ $C_{11}H_{23}OH$ undecyl alcohol (hendecyl alcohol) (661)

(163) $C_{11}H_{24}O$ $(CH_3)_2CH(CH_2)_2C(CH_3)OHCH_2CH(CH_3)_2$ 2,4,7-trimethyl-4-octanol (10)

(164) $C_{12}H_{26}O$ $C_{12}H_{25}OH$ dodecyl alcohol (1-dodecanol) (661)

b. Polyhydric alcohols and sugars

(165) C_2H_5ClO CH_2OHCH_2Cl ethylenechlorohydrin (320, 428)

(166) $C_2H_6O_2$ CH_2OHCH_2OH ethylene glycol (320, 350, 351, 428, 456, 595, 645)

(167) $C_3H_8O_2$ $CH_3CHOHCH_2OH$ α-propylene glycol (1,2-propanediol) (456)

(168) $C_3H_8O_3$ $CH_2OHCHOHCH_2OH$ glycerin (glycerol) (26, 28, 29, 122, 242, 294, 319, 417, 428, 553, 598, 616, 617, 645)

(169) $C_5H_{10}O_4$ $CH_2OHCHOHCH_2OCOCH_3$ glycerol acetate (598)

(170) $C_6H_{12}O_6$ $CH_2OH(CHOH)_4CHO$ glucose (386)

(171) $C_6H_{12}O_6$ $CH_2OH(CHOH)_4CHO$ galactose (386)

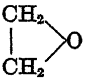
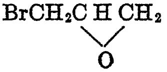
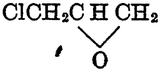
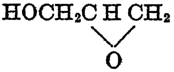
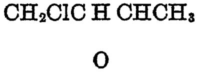
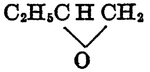
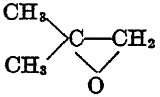
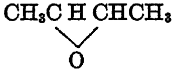
(172) $C_6H_{12}O_6$ $CH_2OH(CHOH)_3COCH_2OH$ fructose (386)

(173) $C_{12}H_{22}O_{11}$ $C_{12}H_{22}O_{11}$ sucrose (386, 516, 645)

(174) $C_{12}H_{22}O_{11} \cdot H_2O$ $C_{12}H_{22}O_{11} \cdot H_2O$ maltose (386)

(175) $C_{18}H_{32}O_{16} \cdot 5H_2O$ $C_{18}H_{32}O_{16} \cdot 5H_2O$ raffinose (386)

IV. *Ethers*

(176)	C_2H_4O		ethylene oxide (266, 409, 410)
(177)	C_2H_6O	CH_3OCH_3	dimethyl ether (173, 176, 266, 569)
(178)	C_3H_5BrO	 $\underset{O}{BrCH_2C\,H\,CH_2}$	bromomethylethylene oxide (409, 410)
(179)	C_3H_5ClO	 $\underset{O}{ClCH_2C\,H\,CH_2}$	chloromethylethylene oxide (409, 410)
(180)	$C_3H_6O_2$	 $\underset{O}{HOCH_2C\,H\,CH_2}$	hydroxymethylethylene oxide (409, 410)
(181)	$C_3H_8O_2$	$CH_2OHCH_2OCH_3$	ethylene glycol monomethyl ether (320)
(182)	C_4H_7ClO	 $\underset{O}{CH_2ClC\,H\,CHCH_3}$	α-chloromethyl-β-methylethylene oxide (409)
(183)	C_4H_8O	 $\underset{O}{C_2H_5C\,H\,CH_2}$	ethylethylene oxide (409, 410)
(184)	C_4H_8O		α,α-dimethylethylene oxide (409, 410)
(185)	C_4H_8O	 $\underset{O}{CH_3C\,H\,CHCH_3}$	α,β-dimethylethylene oxide (409)
(186)	$C_4H_{10}O$	$C_2H_5OC_2H_5$	diethyl ether (25, 162, 166, 168, 170, 171, 192, 194, 242, 294, 452, 523, 529, 530, 561, 569, 597, 654)
(187)	$C_4H_{10}O_2$	$CH_2OHCH_2OC_2H_5$	ethylene glycol monoethyl ether (320)
(188)	$C_5H_{12}O_2$	$CH_2OHCH_2OC_3H_7$	ethylene glycol monopropyl ether (320)
(189)	$C_6H_{14}O$	$C_3H_7OC_3H_7$	dipropyl ether (316)
(190)	$C_6H_{14}O$	$(CH_3)_2CHOCH(CH_3)_2$	diisopropyl ether (316)
(191)	$C_{10}H_{22}O$	$(C_5H_{11})_2O$	diamyl ether (316)
(192)	$C_{10}H_{22}O$	$[(CH_3)_2CHCH_2CH_2]_2O$	diisoamyl ether (316)

V. *Carbonyl compounds*

a. Aldehydes

(193)	CH_2O	CH_2O	formaldehyde (309, 348, 376, 485, 596, 597, 606)
(194)	$(CH_2O)_x$	$(CH_2O)_x$	paraformaldehyde (309)
(195)	C_2H_4O	CH_3CHO	acetaldehyde (155, 161, 348, 500, 627, 668)
(196)	C_3H_6O	C_2H_5CHO	propionaldehyde (155, 161, 162, 166, 348)
(197)	C_4H_8O	C_3H_7CHO	butyraldehyde (348, 456)
(198)	C_4H_8O	$(CH_3)_2CHCHO$	isobutyraldehyde (348)
(199)	$C_4H_8O_2$	$CH_3CHOHCH_2CHO$	aldol (310)
(200)	$C_5H_{10}O$	C_4H_9CHO	valeraldehyde (348)
(201)	$C_5H_{10}O$	$(CH_3)_2CHCH_2CHO$	isovaleraldehyde (348)

(202)	$C_5H_{10}O$	$C_2H_5(CH_3)CHCHO$ *sec*-valeraldehyde (α-methylbutyraldehyde) (348)
(203)	$C_5H_{10}O$	$(CH_3)_3CCHO$ *tert*-valeraldehyde (pivalaldehyde) (348)
(204)	$C_6H_{12}O$	$C_5H_{11}CHO$ caproaldehyde (348)
(205)	$C_6H_{12}O$	$(CH_3)_2CHCH_2CH_2CHO$ isocaproaldehyde (348)
(206)	$C_6H_{12}O$	$C_2H_5(CH_3)_2CCHO$ *tert*-caproaldehyde (α,α-dimethylbutyraldehyde) (348)
(207)	$C_6H_{12}O_3$	$(C_2H_4O)_3$ paraldehyde (434, 500, 627)
(208)	$C_7H_{14}O$	$C_6H_{13}CHO$ heptanal (enanthaldehyde) (348, 414)
(209)	$C_8H_{15}O$	$C_7H_{15}CHO$ octanal (caprylaldehyde) (348)
(210)	$C_9H_{18}O$	$C_8H_{17}CHO$ nonanal (pelargonaldehyde) (348)
(211)	$C_{10}H_{20}O$	$C_9H_{19}CHO$ decanal (capraldehyde) (348)
(212)	$C_{11}H_{22}O$	$C_{10}H_{21}CHO$ undecanal (undecylaldehyde) (90)
(213)	$C_{12}H_{24}O$	$C_{11}H_{23}CHO$ dodecanal (lauraldehyde) (90)
(214)	$C_{12}H_{24}O$	$CH_3(CH_2)_8CH(CH_3)CHO$ α-methylundecanal (α-methylundecylaldehyde) (90)·

1. Halogen derivatives of aldehydes

(215)	C_2HCl_3O	CCl_3CHO chloral (125, 173, 176, 490, 500, 595)
(216)	$C_2H_2Cl_2O$	Cl_2HCCHO dichloroacetaldehyde (125)
(217)	$C_2H_3Cl_3O_2$	$CCl_3CHO \cdot H_2O$ chloral hydrate (490, 500)

b. Ketones

(218)	C_3H_6O	CH_3COCH_3 acetone (152, 158, 163, 167, 170, 194, 206, 242, 294, 348, 500, 541, 561, 568, 574, 596, 597, 606, 644, 645, 646)
(219)	$C_4H_6O_2$	$CH_3COCOCH_3$ diacetyl (298, 358)
(220)	C_4H_8O	$CH_3COC_2H_5$ methyl ethyl ketone (153, 159, 242, 348, 561, 597, 644)
(221)	$C_5H_8O_2$	$CH_3COCH_2COCH_3$ acetylacetone (298, 354, 359)
(222)	$C_5H_{10}O$	$C_2H_5COC_2H_5$ diethyl ketone (242, 348, 597, 644)
(223)	$C_5H_{10}O$	$CH_3COC_3H_7$ methyl propyl ketone (242, 348, 359)
(224)	$C_5H_{10}O$	$CH_3COCH(CH_3)_2$ methyl isopropyl ketone (348)
(225)	$C_6H_{10}O_2$	$CH_3CO(CH_2)_2COCH_3$ acetonylacetone (2,4-hexanedione) (298, 354)
(226)	$C_6H_{10}O_2$	$CH_3COCH(CH_3)COCH_3$ methylacetylacetone (359)
(227)	$C_6H_{12}O$	$CH_3COC_4H_9$ methyl butyl ketone (348)
(228)	$C_6H_{12}O$	$CH_3COCH_2CH(CH_3)_2$ methyl isobutyl ketone (348)
(229)	$C_6H_{12}O$	$CH_3COCH(CH_3)C_2H_5$ methyl *sec*-butyl ketone (348, 359)
(230)	$C_6H_{12}O$	$CH_3COC(CH_3)_3$ methyl *tert*-butyl ketone (348)
(231)	$C_6H_{12}O$	$C_2H_5COC_3H_7$ ethyl propyl ketone (445)
(232)	$C_6H_{12}O$	$C_2H_5COCH(CH_3)_2$ ethyl isopropyl ketone (445)
(233)	$C_7H_{12}O_2$	$CH_3COC(CH_3)_2COCH_3$ dimethylacetylacetone (3,3-dimethyl-2,4-pentanedione) (358, 359)
(234)	$C_7H_{14}O$	$C_3H_7COC_3H_7$ dipropyl ketone (348)
(235)	$C_7H_{14}O$	$(CH_3)_2CHCOCH(CH_3)_2$ diisopropyl ketone (348)
(236)	$C_7H_{14}O$	$CH_3COC_5H_{11}$ methyl amyl ketone (348)
(237)	$C_7H_{14}O$	$CH_3COC(CH_3)_2C_2H_5$ methyl *tert*-amyl ketone (3,3-dimethyl-2-pentanone) (348, 359)

(238)	$C_7H_{14}O$	$C_2H_5COC_4H_9$	ethyl butyl ketone (445)
(239)	$C_7H_{14}O$	$C_2H_5COCH_2CH(CH_3)_2$	ethyl isobutyl ketone (445)
(240)	$C_8H_{16}O$	$CH_3COC_6H_{13}$	methyl hexyl ketone (348)
(241)	$C_8H_{16}O$	$C_2H_5COC_5H_{11}$	ethyl amyl ketone (445)
(242)	$C_8H_{16}O$	$C_2H_5CO(CH_2)_2CH(CH_3)_2$	ethyl isoamyl ketone (445)
(243)	$C_9H_{18}O$	$C_2H_5COC_6H_{13}$	ethyl hexyl ketone (445)
(244)	$C_9H_{18}O$	$C_2H_5CO(CH_2)_3CH(CH_3)_2$	ethyl isohexyl ketone (445)
(245)	$C_9H_{18}O$	$(CH_3)_2CHCH_2COCH_2CH(CH_3)_2$	diisobutyl ketone (348)
(246)	$C_{11}H_{22}O$	$CH_3COC_9H_{19}$	methyl nonyl ketone (348)
(247)	$C_{18}H_{36}O$	$C_2H_5COC_{15}H_{31}$	ethyl pentadecyl ketone (445)

1. Halogen derivatives of ketones

(248)	$C_3H_4Cl_2O$	$Cl_2HCCOCH_3$	1,1-dichloroacetone (125)
(249)	C_3H_5ClO	ClH_2CCOCH_3	chloroacetone (125)

c. Acyl halides

(250)	C_2Cl_4O	Cl_3CCOCl	trichloroacetyl chloride (125)
(251)	C_2HCl_3O	$Cl_2HCCOCl$	dichloroacetyl chloride (125)
(252)	$C_2H_2Cl_2O$	$CH_2ClCOCl$	chloroacetyl chloride (125, 173, 176)
(253)	C_2H_3BrO	CH_3COBr	acetyl bromide (168, 171, 366)
(254)	C_2H_3ClO	CH_3COCl	acetyl chloride (168, 171, 357, 592)
(255)	C_3H_5BrO	C_2H_5COBr	propionyl bromide (366)
(256)	C_3H_5ClO	CH_3CH_2COCl	propionyl chloride (357)
(257)	C_4H_7ClO	$CH_3(CH_2)_2COCl$	butyryl chloride (357)
(258)	C_4H_7ClO	$(CH_3)_2CHCOCl$	isobutyryl chloride (357)
(259)	C_5H_9ClO	$CH_3(CH_2)_3COCl$	valeryl chloride (357)
(260)	C_5H_9ClO	$(CH_3)_2CHCH_2COCl$	isovaleryl chloride (357)
(261)	C_5H_9ClO	$CH_3CH_2CH(CH_3)COCl$	α-methylbutyryl chloride (357)
(262)	C_5H_9ClO	$(CH_3)_3CCOCl$	pivalyl chloride (357)
(263)	$C_6H_{11}ClO$	$CH_3(CH_2)_4COCl$	caproyl chloride (357)
(264)	$C_6H_{11}ClO$	$(CH_3)_2CH(CH_2)_2COCl$	isocaproyl chloride (357)
(265)	$C_6H_{11}ClO$	$C_2H_5C(CH_3)_2COCl$	α,α-dimethylbutyryl chloride (357)
(266)	$C_7H_{10}Cl_2O_2$	$(C_2H_5)_2C(COCl)_2$	diethylmalonyl chloride (358)

VI. Monocarboxylic acids and their derivatives

a. Monocarboxylic acids

(267)	$C_2D_4O_2$	CD_3COOD	acetic acid-d_4 (19)
(268)	CH_2O_2	$HCOOH$	formic acid (28, 48, 152, 158, 168, 171, 242, 294, 352, 428, 489, 535, 625)
(269)	$C_2H_4O_2$	CH_3COOH	acetic acid (19, 33, 152, 157, 158, 168, 170, 171, 194, 221, 237, 242, 248, 294, 330, 352, 378, 379, 380, 403, 490, 535, 546, 547, 548, 561, 597, 618, 645, 663)
(270)	$C_3H_6O_2$	C_2H_5COOH	propionic acid (152, 156, 158, 242, 352, 597, 618)
(271)	$C_4H_8O_2$	C_3H_7COOH	butyric acid (152, 156, 158, 242, 352, 618)

(272)	$C_4H_8O_2$	$(CH_3)_2CHCOOH$	isobutyric acid (352, 373, 672)
(273)	$C_5H_{10}O_2$	C_4H_9COOH	valeric acid (352, 597)
(274)	$C_5H_{10}O_2$	$(CH_3)_2CHCH_2COOH$	isovaleric acid (352, 597)
(275)	$C_5H_{10}O_2$	$(CH_3)_3CCOOH$	pivalic acid (α,α-dimethylpropionic acid) (352)
(276)	$C_5H_{10}O_2$	$C_2H_5CH(CH_3)COOH$	α-methylbutyric acid (352)
(277)	$C_6H_{12}O_2$	$C_5H_{11}COOH$	caproic acid (352)
(278)	$C_6H_{12}O_2$	$(CH_3)_2CHCH_2CH_2COOH$	isocaproic acid (352)
(279)	$C_6H_{12}O_2$	$C_2H_5C(CH_3)_2COOH$	α,α-dimethylbutyric acid (352)
(280)	$C_7H_{14}O_2$	$C_6H_{13}COOH$	enanthic acid (352)
(281)	$C_8H_{16}O_2$	$C_7H_{15}COOH$	caprylic acid (352)
(282)	$C_9H_{18}O_2$	$C_8H_{17}COOH$	pelargonic acid (352)
(283)	$C_{10}H_{20}O_2$	$C_9H_{19}COOH$	capric acid (352)

b. Halogen derivatives of monocarboxylic acids

(284)	$C_2HCl_3O_2$	CCl_3COOH	trichloroacetic acid (248, 352, 490, 592, 664)
(285)	$C_2H_2ClO_2$	$CHCl_2COOH$	dichloroacetic acid (352, 456, 592, 664)
(286)	$C_2H_3BrO_2$	$CH_2BrCOOH$	bromoacetic acid (124)
(287)	$C_2H_3ClO_2$	$CH_2ClCOOH$	chloroacetic acid (248, 352, 490, 592, 664)

c. Ketonic derivatives of monocarboxylic acids

(288)	$C_3H_4O_3$	$CH_3COCOOH$	pyruvic acid (168, 171, 354)

d. Anhydrides of monocarboxylic acids

(289)	$C_4H_6O_3$	$(CH_3CO)_2O$	acetic anhydride (369, 490, 592)
(290)	$C_6H_{10}O_3$	$(C_2H_5CO)_2O$	propionic anhydride (369)
(291)	$C_8H_{14}O_3$	$(C_3H_7CO)_2O$	butyric anhydride (369)
(292)	$C_8H_{14}O_3$	$[(CH_3)_2CHCO]_2O$	isobutyric anhydride (369)
(293)	$C_{10}H_{18}O_3$	$[(CH_3)_2CHCH_2O]_2O$	isovaleric anhydride (369)
(294)	$C_{12}H_{22}O_3$	$(C_5H_{11}CO)_2O$	caproic anhydride (369)

e. Esters of monocarboxylic acids

1. Esters

(295)	$C_2H_4O_2$	$HCOOCH_3$	methyl formate (168, 171, 353, 488, 605)
(296)	$C_3H_6O_2$	$HCOOC_2H_5$	ethyl formate (152, 156, 158, 248, 353, 485, 488)
(297)	$C_3H_6O_2$	CH_3COOCH_3	methyl acetate (124, 152, 156, 158, 170, 194, 353, 488, 597, 605)
(298)	$C_4H_8O_2$	$CH_3COOC_2H_5$	ethyl acetate (124, 152, 156, 158, 165, 194, 248, 353, 488, 490, 561, 597)
(299)	$C_4H_8O_2$	$C_2H_5COOCH_3$	methyl propionate (316, 353, 488, 597, 605)
(300)	$C_4H_8O_2$	$HCOOC_3H_7$	propyl formate (357, 488, 605)
(301)	$C_4H_8O_2$	$HCOOCH(CH_3)_2$	isopropyl formate (357)
(302)	$C_5H_{10}O_2$	$CH_3COOC_3H_7$	propyl acetate (124, 194, 488, 597)
(303)	$C_5H_{10}O_2$	$CH_3COOCH(CH_3)_2$	isopropyl acetate (124)
(304)	$C_5H_{10}O_2$	$C_2H_5COOC_2H_5$	ethyl propionate (152, 158, 353, 488, 561, 597, 605)

(305)	$C_5H_{10}O_2$	$HCOOC_4H_9$ butyl formate (357, 456, 488)
(306)	$C_5H_{10}O_2$	$HCOOCH_2CH(CH_3)_2$ isobutyl formate (357, 605)
(307)	$C_5H_{10}O_2$	$C_3H_7COOCH_3$ methyl butyrate (353, 488)
(308)	$C_5H_{10}O_2$	$HCOOCH(CH_3)C_2H_5$ *sec*-butyl formate (357)
(309)	$C_5H_{10}O_2$	$(CH_3)_2CHCOOCH_3$ methyl isobutyrate (353)
(310)	$C_6H_{12}O_2$	$C_2H_5COOC_3H_7$ propyl propionate (316, 456)
(311)	$C_6H_{12}O_2$	$C_2H_5COOCH(CH_3)_2$ isopropyl propionate (316)
(312)	$C_6H_{12}O_2$	$CH_3COOC_4H_9$ butyl acetate (124, 456, 488, 597, 605)
(313)	$C_6H_{12}O_2$	$CH_3COOCH_2CH(CH_3)_2$ isobutyl acetate (124, 605)
(314)	$C_6H_{12}O_2$	$C_3H_7COOC_2H_5$ ethyl butyrate (152, 158, 353, 488, 561)
(315)	$C_6H_{12}O_2$	$(CH_3)_2CHCOOC_2H_5$ ethyl isobutyrate (353)
(316)	$C_6H_{12}O_2$	$CH_3COOCH(CH_3)C_2H_5$ *sec*-butyl acetate (124)
(317)	$C_6H_{12}O_2$	$HCOO(CH_2)_2CH(CH_3)_2$ isoamyl formate (168, 171, 357, 488, 597)
(318)	$C_6H_{12}O_2$	$C_4H_9COOCH_3$ methyl valerate (353)
(319)	$C_6H_{12}O_2$	$(CH_3)_2CHCH_2COOCH_3$ methyl isovalerate (353)
(320)	$C_6H_{12}O_2$	$C_2H_5CH(CH_3)COOCH_3$ methyl α-methylbutyrate (353)
(321)	$C_6H_{12}O_2$	$HCOOC_5H_{11}$ amyl formate (357)
(322)	$C_6H_{12}O_2$	$(CH_3)_3CCOOCH_3$ methyl pivalate (353)
(323)	$C_7H_{14}O_2$	$CH_3COOC_5H_{11}$ amyl acetate (124)
(324)	$C_7H_{14}O_2$	$CH_3COO(CH_2)_2CH(CH_3)_2$ isoamyl acetate (124, 152, 158, 488)
(325)	$C_7H_{14}O_2$	$C_2H_5COOC_4H_9$ butyl propionate (316)
(326)	$C_7H_{14}O_2$	$C_2H_5COOCH_2CH(CH_3)_2$ isobutyl propionate (316)
(327)	$C_7H_{14}O_2$	$C_4H_9COOC_2H_5$ ethyl valerate (353)
(328)	$C_7H_{14}O_2$	$(CH_3)_2CHCH_2COOC_2H_5$ ethyl isovalerate (353)
(329)	$C_7H_{14}O_2$	$C_2H_5CH(CH_3)COOC_2H_5$ ethyl α-methylbutyrate (353)
(330)	$C_7H_{14}O_2$	$(CH_3)_3CCOOC_2H_5$ ethyl pivalate (353)
(331)	$C_7H_{14}O_2$	$C_5H_{11}COOCH_3$ methyl caproate (353)
(332)	$C_7H_{14}O_2$	$(CH_3)_2CH(CH_2)_2COOCH_3$ methyl isocaproate (353)
(333)	$C_7H_{14}O_2$	$C_2H_5C(CH_3)(CH_3)COOCH_3$ methyl α,α-dimethylbutyrate (353)
(334)	$C_8H_{16}O_2$	$C_2H_5COOC_5H_{11}$ amyl propionate (316)
(335)	$C_8H_{16}O_2$	$C_2H_5COO(CH_2)_2CH(CH_3)_2$ isoamyl propionate (316, 456, 605)
(336)	$C_8H_{16}O_2$	$C_5H_{11}COOC_2H_5$ ethyl caproate (353)
(337)	$C_8H_{16}O_2$	$(CH_3)_2CH(CH_2)_2COOC_2H_5$ ethyl isocaproate (353)
(338)	$C_8H_{16}O_2$	$C_2H_5C(CH_3)(CH_3)COOC_2H_5$ ethyl α,α-dimethyl-butyrate (353)
(339)	$C_8H_{16}O_2$	$C_6H_{13}COOCH_3$ methyl enanthate (353)
(340)	$C_9H_{18}O_2$	$C_6H_{13}COOC_2H_5$ ethyl enanthate (353)
(341)	$C_9H_{18}O_2$	$C_7H_{15}COOCH_3$ methyl caprylate (353)
(342)	$C_{10}H_{20}O_2$	$C_7H_{15}COOC_2H_5$ ethyl caprylate (353)
(343)	$C_{10}H_{20}O_2$	$C_8H_{17}COOCH_3$ methyl pelargonate (353)
(344)	$C_{11}H_{22}O_2$	$C_9H_{19}COOCH_3$ methyl caprate (353)

2. Halogen derivatives of esters

(345)	$C_2H_3ClO_2$	$ClCOOCH_3$ methyl chloroformate (357)
(346)	$C_3H_3Cl_3O_2$	$Cl_3CCOOCH_3$ methyl trichloroacetate (124)

(347)	$C_3H_4Cl_2O_2$	$CHCl_2COOCH_3$	methyl dichloroacetate (124)
(348)	$C_3H_5BrO_2$	$CH_2BrCOOCH_3$	methyl bromoacetate (124, 631)
(349)	$C_3H_5ClO_2$	$ClCOOC_2H_5$	ethyl chloroformate (173, 176, 357)
(350)	$C_3H_5ClO_2$	$CH_2ClCOOCH_3$	methyl chloroacetate (124)
(351)	$C_4H_5Cl_3O_2$	$CCl_3COOC_2H_5$	ethyl trichloroacetate (124)
(352)	$C_4H_6Cl_2O_2$	$CHCl_2COOC_2H_5$	ethyl dichloroacetate (124)
(353)	$C_4H_7BrO_2$	$CH_2BrCOOC_2H_5$	ethyl bromoacetate (124)
(354)	$C_4H_7ClO_2$	$CH_2ClCOOC_2H_5$	ethyl chloroacetate (124, 456, 485)
(355)	$C_4H_7ClO_2$	$ClCOOC_3H_7$	propyl chloroformate (357)
(356)	$C_5H_7Cl_3O_2$	$CCl_3COOC_3H_7$	propyl trichloroacetate (124)
(357)	$C_5H_7Cl_3O_2$	$CCl_3COOCH(CH_3)_2$	isopropyl trichloroacetate (124)
(358)	$C_5H_8Cl_2O_2$	$CHCl_2COOC_3H_7$	propyl dichloroacetate (124)
(359)	$C_5H_8Cl_2O_2$	$CHCl_2COOCH(CH_3)_2$	isopropyl dichloroacetate (124)
(360)	$C_5H_9BrO_2$	$CH_2BrCOOC_3H_7$	propyl bromoacetate (124)
(361)	$C_5H_9BrO_2$	$CH_2BrCOOCH(CH_3)_2$	isopropyl bromoacetate (124)
(362)	$C_5H_9ClO_2$	$CH_2ClCOOC_3H_7$	propyl chloroacetate (124)
(363)	$C_5H_9ClO_2$	$CH_2ClCOOCH(CH_3)_2$	isopropyl chloroacetate (124)
(364)	$C_5H_9ClO_2$	$ClCOOCH_2CH(CH_3)_2$	isobutyl chloroformate (357)
(365)	$C_6H_9Cl_3O_2$	$CCl_3COOC_4H_9$	butyl trichloroacetate (124)
(366)	$C_6H_{10}Cl_2O_2$	$CHCl_2COOC_4H_9$	butyl dichloroacetate (124)
(367)	$C_6H_{11}BrO_2$	$CH_2BrCOOC_4H_9$	butyl bromoacetate (124)
(368)	$C_6H_{11}ClO_2$	$ClCOOCH_2CH_2CH(CH_3)_2$	isoamyl chloroformate (357)
(369)	$C_6H_{11}ClO_2$	$CH_2ClCOOC_4H_9$	butyl chloroacetate (124)
(370)	$C_7H_{11}Cl_3O_2$	$CCl_3COOC_5H_{11}$	amyl trichloroacetate (124)
(371)	$C_7H_{12}Cl_2O_2$	$CHCl_2COOC_5H_{11}$	amyl dichloroacetate (124)
(372)	$C_7H_{13}ClO_2$	$CH_2ClCOOC_5H_{11}$	amyl chloroacetate (124)

3. Ketonic derivatives of esters

(373)	$C_4H_6O_3$	$CH_3COCOOCH_3$	methyl pyruvate (358)
(374)	$C_5H_8O_3$	$CH_3COCH_2COOCH_3$	methyl acetoacetate (358, 444)
(375)	$C_5H_8O_3$	$CH_3COCOOC_2H_5$	ethyl pyruvate (358, 366)
(376)	$C_6H_{10}O_3$	$CH_3COCH(CH_3)COOCH_3$	methyl α-methylacetoacetate (444)
(377)	$C_6H_{10}O_3$	$CH_3COCH_2COOC_2H_5$	ethyl acetoacetate (keto) (165, 358, 485)
(378)	$C_6H_{10}O_3$	$CH_3C(OH){=}CHCOOC_2H_5$	ethyl acetoacetate (enol) (165, 485)
(379)	$C_6H_{10}O_3$	$CH_3CO(CH_2)_2COOCH_3$	methyl levulinate (354)
(380)	$C_7H_{12}O_3$	$CH_3COCH(CH_3)COOC_2H_5$	ethyl α-methylacetoacetate (358, 444)
(381)	$C_7H_{12}O_3$	$CH_3CO(CH_2)_2COOC_2H_5$	ethyl levulinate (354)
(382)	$C_7H_{12}O_3$	$CH_3COCH(C_2H_5)COOCH_3$	methyl α-ethylacetoacetate (444)
(383)	$C_7H_{12}O_3$	$CH_3COC(CH_3)_2COOCH_3$	methyl α,α-dimethylacetoacetate (354, 358)
(384)	$C_8H_{14}O_3$	$CH_3COCH(C_2H_5)COOC_2H_5$	ethyl α-ethylacetoacetate (444)
(385)	$C_8H_{14}O_3$	$CH_3COC(CH_3)_2COOC_2H_5$	ethyl α,α-dimethylacetoacetate (358)

(386)	$C_9H_{16}O_3$	$CH_3COCH(CH_2CH(CH_3)_2)COOCH_3$	methyl α-isoamylacetoacetate (444)
(387)	$C_{10}H_{18}O_3$	$CH_3COCH(C_4H_9)COOC_2H_5$	ethyl α-butylacetoacetate (444)
(388)	$C_{11}H_{20}O_3$	$CH_3COCH(CH_2CH_2CH(CH_3)_2)COOC_2H_5$	ethyl α-isoamylacetoacetate (444)

f. Salts of monocarboxylic acids

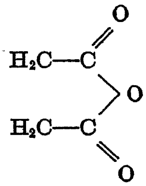
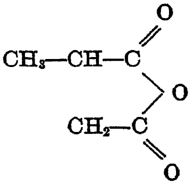
(389)	$CHNaO_2$	$HCOONa$	sodium formate (248)
(390)	$C_2Cl_3NaO_2$	CCl_3COONa	sodium trichloroacetate (248)
(391)	$C_2H_2ClNaO_2$	$CH_2ClCOONa$	sodium chloroacetate (248)
(392)	C_2H_3NaO	CH_3COONa	sodium acetate (162, 166, 248)
(393)	$C_2H_7NO_2$	CH_3COONH_4	ammonium acetate (162, 166, 192, 376)
(394)	$C_4H_6CdO_4$	$(CH_3COO)_2Cd$	cadmium acetate (376)
(395)	$C_4H_6O_4Pb$	$(CH_3COO)_2Pb$	lead acetate (376)
(396)	$C_4H_6O_4Zn$	$(CH_3COO)_2Zn$	zinc acetate (163, 167, 376)

VII. Dicarboxylic acids and their derivatives

a. Dicarboxylic acids

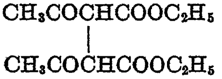
(397)	$C_2H_2O_4$	$(COOH)_2$	oxalic acid (313, 376, 536)
(398)	$C_3H_4O_4$	$CH_2(COOH)_2$	malonic acid (248)
(399)	$C_4H_6O_6$	$HOOC(CHOH)_2COOH$	tartaric acid (502)
(400)	$C_6H_8O_7$	$HOOCC(OH)(CH_2COOH)_2$	citric acid (476)

b. Anhydrides of dicarboxylic acids

(401)	$C_4H_4O_3$		succinic anhydride (369)
(402)	$C_5H_6O_3$		methylsuccinic anhydride (369)

c. Esters of dicarboxylic acids

(403)	$C_3H_6O_3$	$(CH_3O)_2CO$	dimethyl carbonate (168, 171, 354)
(404)	$C_4H_6O_4$	$CH_3OOCCOOCH_3$	dimethyl oxalate (354)
(405)	$C_5H_8O_4$	$CH_3OOCCH_2COOCH_3$	dimethyl malonate (369)
(406)	$C_5H_{10}O_3$	$(C_2H_5O)_2CO$	diethyl carbonate (168, 171, 354)
(407)	$C_6H_{10}O_4$	$C_2H_5OOCCOOC_2H_5$	diethyl oxalate (163, 167, 354, 592)
(408)	$C_6H_{10}O_4$	$CH_3OOC(CH_2)_2COOCH_3$	dimethyl succinate (354)
(409)	$C_7H_{10}O_5$	$(CH_3OOCCH_2)_2CO$	dimethyl acetonedicarboxylate (358)

(410)	$C_7H_{12}O_4$	$C_2H_5OOCCH_2COOC_2H_5$	diethyl malonate (163, 167, 248, 369, 485)
(411)	$C_8H_{14}O_4$	$C_2H_5OOC(CH_2)_2COOC_2H_5$	diethyl succinate (163, 167, 354)
(412)	$C_8H_{14}O_4$	$C_2H_5OOCCH(CH_3)COOC_2H_5$	diethyl methylmalonate (358)
(413)	$C_8H_{14}O_4$	$C_2H_5OOC(CHOH)_2COOC_2H_5$	ethyl tartrate (502)
(414)	$C_9H_{14}O_6$	$CH_3OOCCH_2CH(COOCH_3)CH_2COOCH_3$	trimethyl tricarballylate (354)
(415)	$C_9H_{16}O_4$	$C_2H_5OOCC(CH_3)(CH_3)COOC_2H_5$	diethyl dimethylmalonate (358)
(416)	$C_{10}H_{16}O_6$	$HC(COOC_2H_5)_3$	triethyl methanetricarboxylate (354)
(417)	$C_{12}H_{18}O_6$	 $\begin{array}{c}CH_3COCHCOOC_2H_5\\ \vert \\ CH_3COCHCOOC_2H_5\end{array}$	diethyl diacetylsuccinate (358)
(418)	$C_{13}H_{20}O_8$	$C(COOC_2H_5)_4$	tetraethyl methanetetracarboxylate (354)

d. Salts of dicarboxylic acids

(419)	$C_3H_2O_4Na_2$	$NaOOCCH_2COONa$	sodium malonate (248)
(420)	$C_4H_4Cs_2O_6$	$CsOOC(CHOH)_2COOCs$	cesium tartrate (502)
(421)	$C_4H_4KNaO_6 \cdot 4H_2O$	$KOOC(CHOH)_2COONa$	Rochelle salt (potassium sodium tartrate) (393, 476)
(422)	$C_4H_4K_2O_6$	$KOOC(CHOH)_2COOK$	potassium tartrate (502)
(423)	$C_4H_4Li_2O_6$	$LiOOC(CHOH)_2COOLi$	lithium tartrate (502)
(424)	$C_4H_4Na_2O_6$	$NaOOC(CHOH)_2COONa$	sodium tartrate (502)
(425)	$C_4H_4O_6Rb_2$	$RbOOC(CHOH)_2COORb$	rubidium tartrate (502)
(426)	$C_4H_{12}N_2O_6$	$NH_4OOC(CHOH)_2COONH_4$	ammonium tartrate (502)

VIII. Cyano compounds

a. Cyano derivatives of hydrocarbons (nitriles)

(427)	CHN	HCN	hydrogen cyanide (44, 144, 145, 148, 165, 330, 400, 625)
(428)	C_2N_2	$(CN)_2$	cyanogen (501)
(429)	C_2H_3N	CH_3CN	acetonitrile (145, 148, 163, 167, 320, 400, 485, 498, 668)
(430)	C_3H_5N	C_2H_5CN	propionitrile (169, 172, 320)
(431)	$C_4H_4N_2$	CH_2CNCH_2CN	succinonitrile (145, 148)
(432)	C_4H_7N	C_3H_7CN	butyronitrile (145, 148, 320)
(433)	C_5H_9N	C_4H_9CN	valeronitrile (145, 148)
(434)	C_5H_9N	$(CH_3)_2CHCH_2CN$	isovaleronitrile (145, 148)
(435)	$C_6H_{11}N$	$(CH_3)_2CHCH_2CH_2CN$	isocapronitrile (145, 148)

b. Cyano derivatives of halogen-substituted hydrocarbons

(436)	C_2Cl_3N	Cl_3CCN	trichloroacetonitrile (125)
(437)	C_2HCl_2N	Cl_2HCCN	dichloroacetonitrile (125)
(438)	C_2H_2ClN	ClH_2CCN	chloroacetonitrile (125)

c. Cyano derivatives of acids

(439)	$C_3H_3O_2N$	$CH_2CNCOOH$	cyanoacetic acid (145, 148)

d. Cyano derivatives of esters

(440)	$C_4H_5O_2N$	$CH_2CNCOOCH_3$	methyl cyanoacetate (500)
(441)	$C_5H_7O_2N$	$CH_2CNCOOC_2H_5$	ethyl cyanoacetate (162, 166)

e. Isocyanides

(442)	C_2H_3N	CH_3NC	methyl isocyanide (145, 148, 400)
(443)	C_3H_5N	C_2H_5NC	ethyl isocyanide (145, 148)

f. Thiocyanates

(444)	C_2H_3NS	CH_3SCN	methyl thiocyanate (501)
(445)	C_3H_5NS	C_2H_5SCN	ethyl thiocyanate (145, 148)

g. Isothiocyanates

(446)	C_3H_5NS	C_2H_5NCS	ethyl isothiocyanate (145, 148)
(447)	C_5H_9NS	$(CH_3)_2CHCH_2NCS$	isobutyl isothiocyanate (145, 148)

h. Isocyanates

(448)	C_2H_3NO	CH_3NCO	methyl isocyanate (371)
(449)	C_3H_5NO	C_2H_5NCO	ethyl isocyanate (336, 371)
(450)	C_4H_7NO	$(CH_3)_2CHNCO$	isopropyl isocyanate (336, 371)

IX. Sulfur compounds

a. Mercaptans

(451)	CH_4S	CH_3SH	methyl mercaptan (620, 625)
(452)	C_2H_6S	C_2H_5SH	ethyl mercaptan (620)
(453)	C_3H_8S	C_3H_7SH	propyl mercaptan (620)
(454)	C_3H_8S	$(CH_3)_2CHSH$	isopropyl mercaptan (185, 189)
(455)	$C_4H_{10}S$	C_4H_9SH	butyl mercaptan (620)
(456)	$C_4H_{10}S$	$(CH_3)_2CHCH_2SH$	isobutyl mercaptan (373, 620)
(457)	$C_4H_{10}S$	$C_2H_5CH(CH_3)SH$	*sec*-butyl mercaptan (346, 347)
(458)	$C_4H_{10}S$	$(CH_3)_3CSH$	*tert*-butyl mercaptan (346, 347)
(459)	$C_5H_{12}S$	$CH_3(CH_2)_4SH$	amyl mercaptan (140, 186, 190)
(460)	$C_5H_{12}S$	$(CH_3)_2CHCH_2CH_2SH$	isoamyl mercaptan (186, 190, 593, 620)
(461)	$C_5H_{12}S$	$(CH_3)_2C(SH)C_2H_5$	*tert*-amyl mercaptan (346, 347)
(462)	$C_6H_{14}S$	$CH_3(CH_2)_5SH$	hexyl mercaptan (140)
(463)	$C_7H_{16}S$	$CH_3(CH_2)_6SH$	heptyl mercaptan (140)

b. Thioethers

(464)	C_2H_6S	CH_3SCH_3	dimethyl sulfide (419, 437, 623)
(465)	$C_2H_6S_2$	CH_3SSCH_3	dimethyl disulfide (90, 437, 623)
(466)	$C_2H_6S_3$	CH_3SSSCH_3	dimethyl trisulfide (90, 268)
(467)	C_3H_8S	$CH_3SC_2H_5$	methyl ethyl sulfide (419, 437)
(468)	$C_4H_{10}S$	$C_2H_5SC_2H_5$	diethyl sulfide (419, 437, 591, 593, 623)
(469)	$C_4H_{10}S_2$	$C_2H_5SSC_2H_5$	diethyl disulfide (90, 437, 623)
(470)	$C_4H_{10}S_3$	$C_2H_5SSSC_2H_5$	diethyl trisulfide (90, 268)
(471)	$C_4H_{10}S_4$	$C_2H_5SSSSC_2H_5$	diethyl tetrasulfide (90)
(472)	$C_6H_{14}S$	$C_3H_7SC_3H_7$	dipropyl sulfide (593, 623)
(473)	$C_8H_{18}S$	$C_4H_9SC_4H_9$	dibutyl sulfide (623)
(474)	$C_8H_{18}S$	$[(CH_3)_2CHCH_2]_2S$	diisobutyl sulfide (593, 623)

c. Esters of sulfurous acid

(475)	$C_2H_6O_2S$	$(CH_3O)_2SO$	dimethyl sulfite (419, 437)
(476)	$C_4H_{10}O_3S$	$(C_2H_5O)_2SO$	diethyl sulfite (419, 437, 475)

d. Thio acids

(477)	C_2H_4OS	CH_3COSH	thioacetic acid (366, 593)
(478)	$C_2H_4O_2S$	$CH_2OHCOSH$	thioglycolic acid (593)
(479)	C_3H_6OS	C_2H_5COSH	thiopropionic acid (366)

X. Nitrogen compounds

a. Amines, amides, imides, and oximes

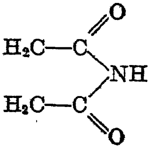
1. Amines

(480)	CH_5N	CH_3NH_2	methylamine (116, 117, 168, 171, 626)
(481)	C_2H_7N	$C_2H_5NH_2$	ethylamine (168, 171, 626)
(482)	C_2H_7N	$(CH_3)_2NH$	dimethylamine (169, 172, 173, 176)
(483)	$C_2H_8N_2$	$NH_2CH_2CH_2NH_2$	ethylenediamine (173, 176, 350, 351)
(484)	C_3H_9N	$(CH_3)_3N$	trimethylamine (173, 176)
(485)	C_3H_9N	$C_3H_7NH_2$	propylamine (173, 176)
(486)	C_3H_9N	$(CH_3)_2CHNH_2$	isopropylamine (185, 189)
(487)	$C_4H_{11}N$	$(CH_3)_2CHCH_2NH_2$	isobutylamine (373)
(488)	$C_4H_{11}N$	$(C_2H_5)_2NH$	diethylamine (173, 176)
(489)	$C_4H_{11}N$	$C_4H_9NH_2$	butylamine (32, 350, 351)
(490)	$C_4H_{11}N$	$C_2H_5CH(CH_3)NH_2$	*sec*-butylamine (32, 346, 347)
(491)	$C_5H_{13}N$	$CH_3(CH_2)_4NH_2$	amylamine (186, 190)
(492)	$C_5H_{13}N$	$(CH_3)_2CH(CH_2)_2NH_2$	isoamylamine (186, 190)
(493)	$C_6H_{15}N$	$(C_2H_5)_3N$	triethylamine (173, 176, 358, 359, 626)
(494)	$C_7H_{17}N$	$C_7H_{15}NH_2$	heptylamine (32)
(495)	NH_3O	NH_2OH	hydroxylamine (428)
(496)	N_2H_4	NH_2NH_2	hydrazine (325, 326, 582)
(497)	N_2H_6O	$NH_2NH_2 \cdot H_2O$	hydrazine hydrate (326, 485, 582)

2. Amides

(498)	CH_2ClNO	$ClCONH_2$	chloroformamide (366)
(499)	CH_3NO	$HCONH_2$	formamide (162, 166, 173, 176, 366, 594)
(500)	CH_4N_2O	NH_2CONH_2	urea (366, 376, 485, 594)
(501)	CH_5ClN_2O	$NH_2CONH_2 \cdot HCl$	urea hydrochloride (377)
(502)	$C_2H_4N_4$	$NH_2C(=NH)NHCN$	dicyanodiamide (173, 176)
(503)	C_2H_5NO	CH_3CONH_2	acetamide (162, 166, 366, 594)
(504)	$C_3H_5NO_2$	$CH_3COCONH_2$	pyruvamide (366)
(505)	C_3H_7NO	$C_2H_5CONH_2$	propionamide (366)
(506)	$C_3H_7NO_2$	$C_2H_5OCONH_2$	ethyl urethan (366)
(507)	$C_4H_9NO_2$	$C_3H_7OCONH_2$	propyl urethan (366)

3. Imides

(508)	$C_4H_5NO_2$		succinimide (369)

4. Oximes

(509)	C_4H_9NO	$CH_3C({=}NOH)C_2H_5$	ethyl methyl ketoxime (87, 88)
(510)	$C_5H_{11}NO$	$CH_3C({=}NOCH_3)C_2H_5$	ethyl methyl ketoxime *O*-methyl ether (87, 88)
(511)	$C_5H_{11}NO$	$CH_3C({=}NOH)C_3H_7$	methyl propyl ketoxime (87, 88)
(512)	$C_6H_{13}NO$	$CH_3C({=}NOH)C_4H_9$	methyl butyl ketoxime (87, 88)

b. Nitro compounds

(513)	CBr_3NO_2	CBr_3NO_2	bromopicrin (442)
(514)	CCl_3NO_2	CCl_3NO_2	chloropicrin (430, 442)
(515)	CHN_3O_9	$CH(NO_3)_3$	trinitromethane (430)
(516)	CH_3NO_2	CH_3NO_2	nitromethane (151, 168, 171, 242, 430, 498)
(517)	$CH_4N_2O_2$	CH_3NHNO_2	methylnitramine (173, 176)
(518)	$C_2H_5NO_2$	$C_2H_5NO_2$	nitroethane (151)
(519)	$C_3H_7NO_2$	$C_3H_7NO_2$	nitropropane (151)
(520)	$C_4H_9NO_2$	$C_4H_9NO_2$	nitrobutane (151)
(521)	$C_5H_{11}NO_2$	$C_5H_{11}NO_2$	nitropentane (151)
(522)	CN_4O_8	$C(NO_2)_4$	tetranitromethane (242, 430, 442)

c. Nitrites

(523)	CH_3NO_2	CH_3ONO	methyl nitrite (151, 170)
(524)	$C_2H_5NO_2$	C_2H_5ONO	ethyl nitrite (151)
(525)	$C_3H_7NO_2$	C_3H_7ONO	propyl nitrite (151)
(526)	$C_4H_9NO_2$	C_4H_9ONO	butyl nitrite (151)
(527)	$C_4H_9NO_2$	$(CH_3)_2CHCH_2ONO$	isobutyl nitrite (373)
(528)	$C_5H_{11}NO_2$	$(CH_3)_2CH(CH_2)_2ONO$	isoamyl nitrite (151)

d. Nitrates

(529)	CH_3NO_3	CH_3ONO_2	methyl nitrate (151, 240, 241, 429)
(530)	$C_2H_5NO_3$	$C_2H_5ONO_2$	ethyl nitrate (151, 241, 429)
(531)	$C_3H_7NO_3$	$C_3H_7ONO_2$	propyl nitrate (151, 241, 429)
(532)	$C_3H_7NO_3$	$(CH_3)_2CHONO_2$	isopropyl nitrate (241)
(533)	$C_4H_9NO_3$	$(CH_3)_2CHCH_2ONO_2$	isobutyl nitrate (373)
(534)	$C_4H_9NO_3$	$C_4H_9ONO_2$	butyl nitrate (151, 429)
(535)	$C_4H_9NO_3$	$C_2H_5CH(CH_3)ONO_2$	*sec*-butyl nitrate (241)
(536)	$C_5H_{11}NO_3$	$C_5H_{11}ONO_2$	amyl nitrate (429, 592)
(537)	$C_5H_{11}NO_3$	$(CH_3)_2CH(CH_2)_2ONO_2$	isoamyl nitrate (241, 592)
(538)	$C_6H_{13}NO_3$	$C_6H_{13}ONO_2$	hexyl nitrate (429)
(539)	$C_7H_{15}NO_3$	$C_7H_{15}ONO_2$	heptyl nitrate (429)
(540)	$C_9H_{19}NO_3$	$C_9H_{19}ONO_2$	nonyl nitrate (431)
(541)	$C_{10}H_{21}NO_3$	$C_{10}H_{21}ONO_2$	decyl nitrate (431)
(542)	$C_{12}H_{25}NO_3$	$C_{12}H_{25}ONO_2$	dodecyl nitrate (431)

XI. Metallo derivatives of hydrocarbons

(543)	CH_3BrMg	CH_3MgBr	methylmagnesium bromide (129)
(544)	CH_3IMg	CH_3MgI	methylmagnesium iodide (129)
(545)	C_2H_6Hg	$Hg(CH_3)_2$	mercury dimethyl (269)
(546)	C_2H_6Zn	$Zn(CH_3)_2$	zinc dimethyl (269, 619)
(547)	C_3H_9Bi	$Bi(CH_3)_3$	bismuth trimethyl (269)

(548)	$C_4H_{10}Hg$	$Hg(C_2H_5)_2$	mercury diethyl (269)
(549)	$C_4H_{10}Zn$	$Zn(C_2H_5)_2$	zinc diethyl (269, 619)
(550)	$C_4H_{12}O_4Si$	$SiO_4(CH_3)_4$	methyl orthosilicate (560)
(551)	$C_4H_{12}Pb$	$Pb(CH_3)_4$	lead tetramethyl (210)
(552)	$C_4H_{12}Si$	$Si(CH_3)_4$	silicon tetramethyl (533)
(553)	$C_4H_{12}Sn$	$Sn(CH_3)_4$	tin tetramethyl (269)
(554)	C_4NiO_4	$Ni(CO)_4$	nickel carbonyl (210, 649)
(555)	C_5FeO_5	$Fe(CO)_5$	iron carbonyl (210)
(556)	$C_6H_{18}O_7Si_2$	$Si_2O_7(CH_3)_6$	methyl ester of silicic (dimeric) acid (560)
(557)	$C_6H_{20}Pb$	$Pb(C_2H_5)_4$	lead tetraethyl (209, 210, 269)
(558)	$C_8H_{24}O_{10}Si_3$	$Si_3O_{10}(CH_3)_8$	methyl ester of silicic (trimeric) acid (560)
(559)	$C_{22}H_{66}O_{30}Si_{10}$	$Si_{10}O_{30}(CH_3)_{22}$	methyl ester of silicic (decameric) acid (560)

B. UNSATURATED COMPOUNDS

I. Hydrocarbons

a. Olefins

(560)	C_2H_4	$CH_2{=}CH_2$	ethylene (99, 194, 195, 196, 197, 205, 405, 411, 650)
(561)	C_3H_6	$CH_3CH{=}CH_2$	propylene (propene) (69, 99)
(562)	C_4H_8	$C_2H_5CH{=}CH_2$	butylene (1-butene) (99)
(563)	C_5H_{10}	$C_3H_7CH{=}CH_2$	amylene (1-pentene) (73, 97, 99, 508)
(564)	C_5H_{10}	$C_2H_5CH{=}CHCH_3$	2-pentene (508)
(565)	C_5H_{10}	$(CH_3)_2C{=}CHCH_3$	trimethylethylene (2-methyl-2-butene) (106, 232)
(566)	C_5H_{10}	$(CH_3)_2CHCH{=}CH_2$	3-methyl-1-butene (635)
(567)	C_6H_{12}	$C_4H_9CH{=}CH_2$	1-hexene (97, 99, 406, 508, 544)
(568)	C_6H_{12}	$(CH_3)_2C{=}C(CH_3)_2$	tetramethylethylene (300, 508, 544)
(569)	C_6H_{12}	$C_3H_7CH{=}CHCH_3$	*cis*-2-hexene (508, 544)
(570)	C_6H_{12}	$C_3H_7CH{=}CHCH_3$	*trans*-2-hexene (508, 544)
(571)	C_6H_{12}	$(CH_3)_2CHCH{=}CHCH_3$	*cis*-4-methyl-2-pentene (281, 508, 544)
(572)	C_6H_{12}	$(CH_3)_2CHCH{=}CHCH_3$	*trans*-4-methyl-2-pentene (508, 544)
(573)	C_6H_{12}	$C_2H_5C(CH_3){=}CHCH_3$	3-methyl-2-pentene (508, 544, 551)
(574)	C_6H_{12}	$C_2H_5CH{=}C(CH_3)_2$	2-methyl-2-pentene (508, 544)
(575)	C_7H_{14}	$C_5H_{11}CH{=}CH_2$	1-heptene (97, 99, 406)
(576)	C_8H_{16}	$C_6H_{13}CH{=}CH_2$	1-octene (97, 99)
(577)	C_8H_{16}	$CH_3C(CH_3)_2CH{=}C(CH_3)_2$	2,4,4-trimethyl-2-pentene (533)
(578)	C_8H_{16}	$C_5H_{11}CH{=}CHCH_3$	2-octene (281)
(579)	C_8H_{16}	$CH_3C(CH_3)_2CH_2C(CH_3){=}CH_2$	2,4,4-trimethyl-1-pentene (533)
(580)	C_8H_{16}	$CH_3CH(CH_3)CH_2C(CH_3){=}CHCH_3$	3,5-dimethyl-2-hexene (10)
(581)	C_8H_{16}	$(CH_3)_2CHCH_2CH{=}C(CH_3)CH_3$	2,5-dimethyl-2-hexene (10)

(582) C_9H_{18} $C_6H_{13}C(CH_3){=}CH_2$ 2-methyl-1-octene (273, 282)
(583) C_9H_{18} $C_5H_{11}CH{=}C(CH_3)_2$ 2-methyl-2-octene (273, 282)
(584) C_9H_{18} $C_7H_{15}CH{=}CH_2$ 1-nonene (97, 99)
(585) C_9H_{18} $C_6H_{13}CH{=}CHCH_3$ 2-nonene (281)
(586) C_9H_{18} $C_5H_{11}C(CH_3){=}CHCH_3$ 3-methyl-2-octene (282)
(587) C_9H_{18} $(CH_3)_2CHCH_2C(CH_3){=}CHC_2H_5$ 4,6-dimethyl-3-heptene (10)
(588) C_9H_{18} $(CH_3)_2CH(CH_2)_2C(CH_3){=}CHCH_3$ 3,6-dimethyl-2-heptene (10)
(589) C_9H_{18} $(CH_3)_2CHCH_2C(CH_3){=}C(CH_3)_2$ 2,3,5-trimethyl-2-hexene (10)
(590) $C_{10}H_{20}$ $C_6H_{13}C(C_2H_5){=}CH_2$ 2-ethyl-1-octene (273)
(591) $C_{10}H_{20}$ $C_6H_{13}C(CH_3){=}CHCH_3$ 3-methyl-2-nonene (273)
(592) $C_{10}H_{20}$ $C_5H_{11}CH{=}C(CH_3)C_2H_5$ 3-methyl-3-nonene (273)
(593) $C_{10}H_{20}$ $C_4H_9CH(CH_3)CH{=}C(CH_3)_2$ 2,4-dimethyl-2-octene (10)
(594) $C_{10}H_{20}$ $(CH_3)_2CHCH_2C(CH_3){=}CHCH(CH_3)_2$ 2,4,6-trimethyl-3-heptene (10)
(595) $C_{11}H_{22}$ $(CH_3)_2CHCH_2CH{=}C(CH_3)CH_2CH(CH_3)_2$ 2,4,7-trimethyl-4-octene (10)

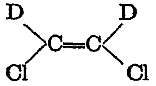
b. Diolefins

(596) C_3H_4 $CH_2{=}C{=}CH_2$ allene (105, 106, 116, 371)
(597) C_4H_6 $CH_2{=}C{=}CHCH_3$ methylallene (1,2-butadiene) (106)
(598) C_4H_6 $CH_2{=}CHCH{=}CH_2$ butadiene (1,3-butadiene) (165)
(599) C_5H_8 $CH_2{=}CHCH_2CH{=}CH_2$ 1,4-pentadiene (508)
(600) C_5H_8 $(CH_3)_2C{=}C{=}CH_2$ 1,1-dimethylallene (3-methyl-1,2-butadiene) (105, 106)
(601) C_5H_8 $CH_3CH{=}C{=}CHCH_3$ 1,3-dimethylallene (2,3-pentadiene) (371)
(602) C_5H_8 $CH_3CH{=}CHCH{=}CH_2$ 1,3-pentadiene (piperylene) (165)
(603) C_5H_8 $CH_2{=}C(CH_3)CH{=}CH_2$ 3-methyl-1,3-butadiene (isoprene) (100,106, 165, 580)
(604) C_5H_8 $CH_2{=}C{=}CHC_2H_5$ ethylallene (1,2-pentadiene) (371)
(605) $(C_5H_8)x$ $(C_5H_8)x$ rubber (246)
(606) C_6H_{10} $C_3H_7CH{=}C{=}CH_2$ propylallene (1,2-hexadiene) (105, 106)
(607) C_6H_{10} $CH_2{=}CHCH_2CH_2CH{=}CH_2$ 1,5-hexadiene (508)
(608) C_6H_{10} $CH_2{=}C(CH_3)C(CH_3){=}CH_2$ 2,3-dimethyl-1,3-butadiene (165)
(609) C_7H_{12} $C_4H_9CH{=}C{=}CH_2$ butylallene (1,2-heptadiene) (105, 106)
(610) $C_{40}H_{56}$ lycopene (228)

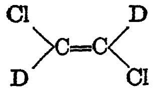
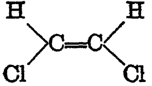
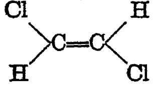
II. Halogen derivatives of hydrocarbons

a. Chlorine derivatives

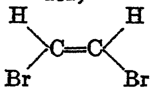
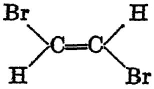
(611) $C_2D_2Cl_2$



cis-1,2-dichloroethylene-d_2 (609)

(612) $C_2D_2Cl_2$		*trans*-1,2-dichloroethylene-d_2 (609)
(613) C_2Cl_4	$CCl_2=CCl_2$	tetrachloroethylene (162, 166, 456, 518, 519, 595)
(614) C_2HCl_3	$CCl_2=CHCl$	trichloroethylene (72, 162, 166, 294)
(615) $C_2H_2Cl_2$	$CHCl=CHCl$	1,2-dichloroethylene (mixt.) (68, 162, 166, 519)
(616) $C_2H_2Cl_2$		1,2-dichloroethylene (*cis*) (72, 77, 78, 494, 495, 496, 600, 608, 609)
(617) $C_2H_2Cl_2$		1,2-dichloroethylene (*trans*) (72, 77, 78, 494, 495, 496, 600, 608, 609)
(618) C_2H_3Cl	$CH_2=CHCl$	vinyl chloride (99, 495, 496, 642)
(619) C_3H_5Cl	$CH_2=CHCH_2Cl$	allyl chloride (3-chloro-1-propene) (57, 99, 162, 166, 297, 495, 496, 500, 554, 578, 642)
(620) C_3H_5Cl	$CHCl=CHCH_3$	1-chloropropylene (1-chloro-1-propene) (495, 496, 642)
(621) C_3H_5Cl	$CH_2=CClCH_3$	2-chloropropylene (2-chloro-1-propene) (495, 496, 642)
(622) $C_4H_6Cl_2$	$CH_3CH=CHCHCl_2$	1,1-dichloro-2-butene (333)
(623) $C_4H_6Cl_2$	$CH_3CHClCH=CHCl$	1,3-dichloro-1-butene (333)
(624) C_4H_7Cl	$CH_2ClCH=CHCH_3$	1-chloro-2-butene (crotyl chloride) (281)

b. Bromine derivatives

(625) $C_2H_2Br_2$	$CHBr=CHBr$	1,2-dibromoethylene (mixt.) (134, 180, 181)
(626) $C_2H_2Br_2$		1,2-dibromoethylene (*cis*) (180, 181)
(627) $C_2H_2Br_2$		1,2-dibromoethylene (*trans*) (180, 181)
(628) C_2H_3Br	$CH_2=CHBr$	vinyl bromide (99)
(629) $C_3H_4Br_2$	$CH_2=CBrCH_2Br$	2,3-dibromo-1-propene (371, 409)
(630) C_3H_5Br	$CH_2=CHCH_2Br$	allyl bromide (57, 99, 162, 166, 295)
(631) $C_4H_6Br_2$	$CH_3CH=CBrCH_2Br$	1,2-dibromo-2-butene (282)
(632) C_4H_7Br	$CH_3CH=CHCH_2Br$	2-butenyl bromide (*cis-trans*) (1-bromo-2-butene) (283, 284)
(633) C_4H_7Br	$CH_2=CHCHBrCH_3$	methylallyl bromide (3-bromo-1-butene) (283, 284)
(634) C_4H_7Br	$CH_3CBr=CHCH_3$	2-bromo-2-butene (282)
(635) C_5H_9Br	$(CH_3)_2C=CBrCH_3$	bromomethylbutene (2-bromo-3-methyl-2-butene) (106)

III. Alcohols

(636)	C_3H_5ClO	$CHCl{=}CHCH_2OH$	3-chloro-2-propen-1-ol (333)
(637)	C_3H_6O	$CH_2{=}CHCH_2OH$	allyl alcohol (2-propen-1-ol) (69, 99, 163, 167, 242, 629)
(638)	C_4H_8O	$CH_3CH{=}CHCH_2OH$	crotonyl alcohol (2-buten-1-ol) (283, 284)
(639)	C_4H_8O	$CH_2{=}CHCH(CH_3)OH$	methylallyl alcohol (3-buten-2-ol) (99, 283, 284)
(640)	$C_5H_{10}O$	$CH_2{=}CHCH(C_2H_5)OH$	ethylallyl alcohol (1-penten-3-ol) (283, 371)
(641)	$C_5H_{10}O$	$CH_3CH{=}C(CH_3)CH_2OH$	methylcrotonyl alcohol (2-methyl-2-buten-1-ol) (288)
(642)	$C_{10}H_{18}O$	$(CH_3)_2C{=}CHCH_2CH_2C(OH)(CH_3)CH{=}CH_2$	linalool (86)
(643)	$C_{10}H_{18}O$	$(CH_3)_2C{=}CHCH_2CH_2C(CH_3){=}CHCH_2OH$	geraniol and nerol (86, 302)
(644)	$C_{10}H_{20}O$	$CH_2OHCH_2CH(CH_3)(CH_2)_3C(CH_3){=}CH_2$	citronellol (86, 273, 469, 470)
(645)	$C_{10}H_{20}O$	$CH_2OHCH_2CH(CH_3)(CH_2)_2CH{=}C(CH_3)_2$	rhodinol (86, 273, 469, 470)

IV. Ethers

a. Halogen derivatives of ethers

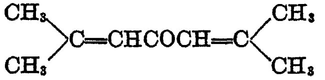
(646)	$C_6H_{11}ClO$	$CH_3CH(OC_2H_5)CH{=}CHCl$	1-chloro-3-ethoxy-1-butene (333)

V. Carbonyl compounds

a. Aldehydes

(647)	C_3H_4O	$CH_2{=}CHCHO$	acrolein (99, 100)
(648)	C_4H_6O	$CH_3CH{=}CHCHO$	crotonaldehyde (283, 284, 310, 366)
(649)	C_4H_6O	$CH_3CH{=}CHCHO$	*trans*-crotonaldehyde (100)
(650)	$C_6H_{10}O$	$C_2H_5CH{=}C(CH_3)CHO$	α-methyl-α-pentenaldehyde (282)
(651)	$C_{10}H_{16}O$	$(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CHCHO$	citral (86)
(652)	$C_{10}H_{18}O$	$CH_2{=}C(CH_3)(CH_2)_3CH(CH_3)CH_2CHO$	citronellal (86, 470)
(653)	$C_{11}H_{20}O$	$C_8H_{17}CH{=}CHCHO$	undecylenaldehyde (90)

b. Ketones

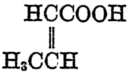
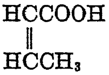
(654)	C_5H_8O	$CH_3CH{=}CHCOCH_3$	ethylideneacetone (366)
(655)	$C_6H_{10}O$	$(CH_3)_2C{=}CHCOCH_3$	mesityl oxide (354, 359)
(656)	$C_9H_{14}O$	 $(CH_3)_2C{=}CHCOCH{=}C(CH_3)_2$	phorone (90)

c. Acyl halides

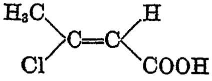
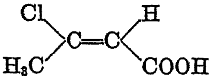
(657)	C_4H_5ClO	$CH_3CH{=}CHCOCl$	crotonyl chloride (366)

VI. Monocarboxylic acids

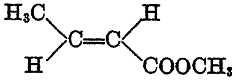
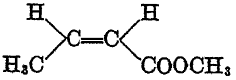
a. Monocarboxylic acids

(658)	$C_3H_4O_2$	$CH_2{=}CHCOOH$	acrylic acid (99)
(659)	$C_4H_6O_2$	 $\begin{array}{c}HCCOOH\\ \|\\ H_3CCH\end{array}$	crotonic acid (*trans*) (180, 181)
(660)	$C_4H_6O_2$	 $\begin{array}{c}HCCOOH\\ \|\\ HCCH_3\end{array}$	crotonic acid (*cis*) (180, 181)
(661)	$C_{10}H_{18}O_2$	$CH_2{=}C(CH_3)(CH_2)_3CH(CH_3)CH_2COOH$	citronellic acid (470)

b. Halogen derivatives of monocarboxylic acids

(662)	$C_4H_5ClO_2$		β-chlorocrotonic acid (*trans*) (180, 181)
(663)	$C_4H_5ClO_2$		β-chlorocrotonic acid (*cis*) (180, 181)

c. Esters of monocarboxylic acids

(664)	$C_4H_6O_2$	$CH_2{=}CHCOOCH_3$	methyl acrylate (366)
(665)	$C_4H_7ClO_2$	$CH_3COOCH_2CH{=}CHCl$	γ-chloroallyl acetate (333)
(666)	$C_5H_8O_2$		methyl crotonate (*trans*) (180, 181)
(667)	$C_5H_8O_2$	$CH_3COOCH_2CH{=}CH_2$	allyl acetate (508)
(668)	$C_5H_8O_2$		methyl crotonate (*cis*) (180, 181)
(669)	$C_6H_9ClO_2$	$CH_3C(Cl){=}CHCOOC_2H_5$	ethyl β-chlorocrotonate (366)
(670)	$C_6H_{10}O_2$	$CH_3COOCH(CH_3)CH{=}CH_2$	methylvinylcarbinol acetate (α-methylallyl acetate) (283)
(671)	$C_6H_{10}O_2$	$CH_3CH{=}CHCOOC_2H_5$	ethyl crotonate (366)
(672)	$C_6H_{10}O_2$	$CH_3COOCH_2CH{=}CHCH_3$	crotonyl acetate (283, 284)
(673)	$C_6H_{10}O_2$	$(CH_3)_2C{=}CHCOOCH_3$	methyl β,β-dimethylacrylate (354)
(674)	$C_6H_{10}O_3$	$CH_3C(OH){=}CHCOOC_2H_5$	ethyl acetoacetate (enol) (165, 485)
(675)	$C_7H_{12}O_2$	$CH_3COOCH_2C(CH_3){=}CHCH_3$	β-methylcrotonyl acetate (288)
(676)	$C_8H_{14}O_3$	$CH_3C(OC_2H_5){=}CHCOOC_2H_5$	ethyl β-ethoxycrotonate (358)

VII. Esters of aminocarboxylic acids

(677) $C_6H_{11}NO_2$ $CH_3C(NH_2){=}CHCOOC_2H_5$ ethyl β-aminocrotonate (358)

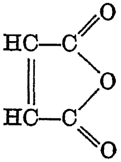
(678) $C_7H_{13}NO_2$ $CH_3C(NHCH_3){=}CHCOOC_2H_5$ ethyl β-methylaminocrotonate (358)

(679) $C_8H_{15}NO_2$ $CH_3C[N(CH_3)_2]{=}CHCOOC_2H_5$ ethyl-β-dimethylaminocrotonate (358)

VIII. Dicarboxylic acids

a. Anhydrides of dicarboxylic acids

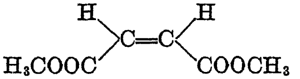
(680) $C_4H_2O_3$



maleic anhydride (369)

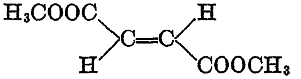
b. Esters of dicarboxylic acids

(681) $C_6H_8O_4$



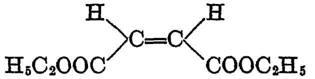
dimethyl maleate (180, 181, 369)

(682) $C_6H_8O_4$



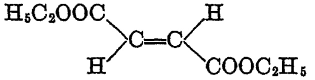
dimethyl fumarate (180, 181)

(683) $C_8H_{12}O_4$



diethyl maleate (180, 181, 231)

(684) $C_8H_{12}O_4$

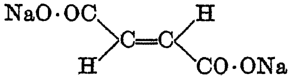


diethyl fumarate (180, 181, 231)

(685) $C_{12}H_{18}O_6$ $C_2H_5OOCCH_2C(COOC_2H_5){=}CHCOOC_2H_5$ triethyl aconitate (354)

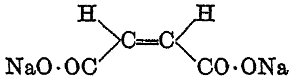
c. Salts of dicarboxylic acids

(686) $C_4H_2Na_2O_4$



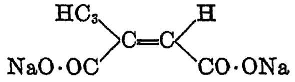
disodium fumarate (603)

(687) $C_4H_2Na_2O_4$



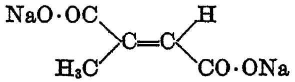
disodium maleate (603)

(688) $C_5H_4Na_2O_4$



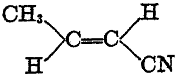
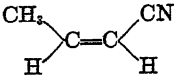
disodium citraconate (603)

(689) $C_5H_4Na_2O_4$



disodium mesaconate (603)

IX. Cyano compounds

(690) C_4H_5N	$CH_2{=}CHCH_2CN$	vinyl acetonitrile (306)
(691) C_4H_5N		crotononitrile (*trans*) (306)
(692) C_4H_5N		crotononitrile (*cis*) (306)
(693) C_4H_5N	$CH_2{=}CHCH_2NCS$	allyl isothiocyanate (162, 166, 592)

X. Thioethers

(694) C_4H_6S	$(CH_2{=}CH)_2S$	divinyl sulfide (69, 89, 94)
(695) $C_6H_{10}S$	$(CH_2{=}CHCH_2)_2S$	diallyl sulfide (69, 89, 94, 591, 593, 623, 625)

XI. Amides

(696) $C_6H_{11}NO$	$CH_3CH{=}CHCON(CH_3)_2$	*N*,*N*-dimethylcrotonamide (366)

XII. Acetylenic compounds

a. Hydrocarbons

(697) C_2DH	$CH \equiv CD$	acetylene-d (583)
(698) C_2D_2	$DC \equiv CD$	acetylene-d_2 (252, 254, 256, 455, 583)
(699) C_2H_2	$CH \equiv CH$	acetylene (45, 46, 194, 195, 196, 197, 200, 252, 255, 303, 411, 455, 476, 555, 615)
(700) C_3H_4	$CH_3C \equiv CH$	methylacetylene (propine) (250, 251)
(701) C_4H_4	$CH_2{=}CHC \equiv CH$	vinylacetylene (1-buten-3-ine) (251)
(702) C_4H_6	$CH_3C \equiv CCH_3$	dimethylacetylene (2-butine) (251, 275, 280)
(703) C_5H_8	$C_2H_5C \equiv CCH_3$	methylethylacetylene (2-pentine) (275, 280)
(704) C_6H_{10}	$C_4H_9C \equiv CH$	butylacetylene (1-hexine) (102, 103)
(705) C_6H_{10}	$C_3H_7C \equiv CCH_3$	methylpropylacetylene (2-hexine) (275 280)
(706) C_6H_{10}	$(CH_3)_2CHCH_2C \equiv CH$	isobutylacetylene (4-methyl-1-pentine) (280)
(707) C_7H_{12}	$C_5H_{11}C \equiv CH$	amylacetylene (1-heptine) (102, 103)
(708) C_7H_{12}	$C_4H_9C \equiv CCH_3$	methylbutylacetylene (2-heptine) (275, 280)
(709) C_8H_{14}	$C_6H_{13}C \equiv CH$	hexylacetylene (1-octine) (102, 103)
(710) C_8H_{14}	$C_5H_{11}C \equiv CCH_3$	methylamylacetylene (2-octine) (102, 103, 274, 280)
(711) C_9H_{12}	$HC \equiv C(CH_2)_5C \equiv CH$	1,8-nonadiine (280)
(712) C_9H_{16}	$C_5H_{11}C \equiv CC_2H_5$	ethylamylacetylene (3-nonine) (274)
(713) C_9H_{16}	$C_6H_{13}C \equiv CCH_3$	methylhexylacetylene (2-nonine) (274, 280)
(714) $C_{10}H_{18}$	$C_5H_{11}C \equiv CC_3H_7$	propylamylacetylene (4-decine) (274)
(715) $C_{10}H_{18}$	$C_6H_{13}C \equiv CC_2H_5$	ethylhexylacetylene (3-decine) (274)

(716) $C_{11}H_{20}$ $C_5H_{11}C{\equiv}CC_4H_9$ butylamylacetylene (5-undecine) (274)

(717) $C_{11}H_{20}$ $C_6H_{13}C{\equiv}CC_3H_7$ propylhexylacetylene (4-undecine) (274)

(718) $C_{12}H_{22}$ $C_6H_{13}C{\equiv}CC_4H_9$ butylhexylacetylene (5-dodecine) (274)

b. Halogen derivatives

(719) C_2I_2 $CI{\equiv}CI$ diiodoacetylene (254)

c. Alcohols

(720) C_3H_4O $CH{\equiv}CCH_2OH$ propargyl alcohol (277, 280)

(721) C_5H_8O $CH{\equiv}CC(CH_3)_2OH$ dimethylpropargyl alcohol (2-methyl-3-butin-2-ol) (102, 103)

(722) $C_8H_{14}O$ $C_5H_{11}C{\equiv}CCH_2OH$ 2-octin-1-ol (276)

(723) $C_9H_{16}O$ $C_6H_{13}C{\equiv}CCH_2OH$ 2-nonin-1-ol (276)

(724) $C_{10}H_{18}O$ $C_5H_{11}C{\equiv}CCHOHCH_3$ 3-nonin-2-ol (276)

(725) $C_{10}H_{18}O$ $C_5H_{11}C{\equiv}CC(OH)(CH_3)CH_3$ 2-methyl-3-nonin-2-ol (280)

(726) $C_{10}H_{18}O$ $C_6H_{13}C{\equiv}CCHOHCH_3$ 3-decin-2-ol (276, 280)

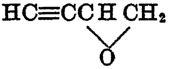
(727) $C_{11}H_{20}O$ $C_5H_{11}C{\equiv}CC(OH)(CH_3)C_2H_5$ 3-methyl-4-decin-3-ol (280)

(728) $C_{14}H_{24}O$ $(C_5H_{11}C{\equiv}C)_2CHOH$ diheptinylcarbinol (280)

(729) $C_{22}H_{34}O$ $(C_5H_{11}C{\equiv}C)_3COH$ triheptinylcarbinol (280)

d. Ethers

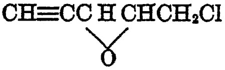
(730) C_4H_4O



$HC{\equiv}CCH\,CH_2$ (with O bridging CH and CH_2) 3,4-epoxy-1-butine (280, 409, 410)

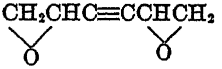
(731) C_4H_6O $CH{\equiv}CCH_2OCH_3$ 3-methoxy-1-propine (277, 280)

(732) C_5H_5ClO



$CH{\equiv}CC\,H\,CHCH_2Cl$ 3,4-epoxy-5-chloro-1-pentine (280, 409)

(733) $C_6H_6O_2$



$CH_2CHC{\equiv}CCHCH_2$ 1,2,5,6-diepoxy-3-hexine (280, 409, 410)

(734) $C_9H_{16}O$ $C_5H_{11}C{\equiv}CCH_2OCH_3$ 1-methoxy-2-octine (277, 280)

(735) $C_{10}H_{18}O$ $C_6H_{13}C{\equiv}CCH_2OCH_3$ 1-methoxy-2-nonine (277, 280)

(736) $C_{10}H_{18}O$ $C_5H_{11}C{\equiv}CCH(OCH_3)CH_3$ 2-methoxy-3-nonine (277, 280)

(737) $C_{11}H_{20}O$ $C_5H_{11}C{\equiv}CC(OCH_3)(CH_3)_2$ 2-methoxy-2-methyl-3-nonine (280)

(738) $C_{11}H_{22}O$ $C_5H_{11}C{\equiv}CC(OCH_3)(CH_3)C_2H_5$ 3-methoxy-3-methyl-4-decine (280)

e. Esters of acetylenic acids

(739) $C_9H_{14}O_2$ $C_5H_{11}C{\equiv}CCOOCH_3$ methyl α-octinoate (102, 103)

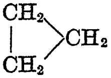
(740) $C_{10}H_{16}O_2$ $C_6H_{13}C{\equiv}CCOOCH_3$ methyl α-noninoate (280)

PART II. CYCLIC COMPOUNDS

A. ALICYCLIC COMPOUNDS

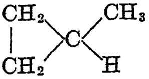
I. Cycloparaffins

(741) C_3H_6



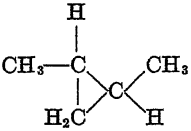
cyclopropane (54, 118, 349, 406, 407, 650, 668)

(742) C_4H_8



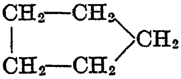
methylcyclopropane (118, 407)

(743) C_5H_{10}



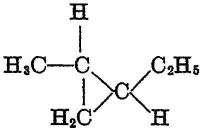
1, 2-dimethylcyclopropane (407)

(744) C_5H_{10}



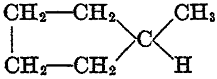
cyclopentane (118, 634, 635, 636)

(745) C_6H_{12}



1-methyl-2-ethylcyclopropane (406, 407)

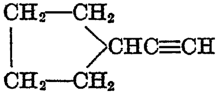
(746) C_6H_{12}



methylcyclopentane (118)

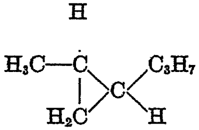
C_6H_{12} (See Sections *V* and *VI* for cyclohexane and derivatives)

(747) C_7H_{10}



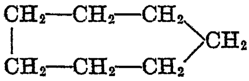
cyclopentylacetylene (278, 280)

(748) C_7H_{14}



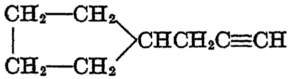
1-methyl-2-propylcyclopropane (407)

(749) C_7H_{14}



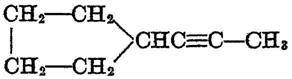
cycloheptane (118)

(750) C_8H_{12}



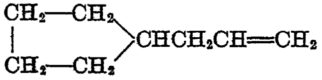
3-cyclopentyl-1-propine (279, 280)

(751) C_8H_{12}

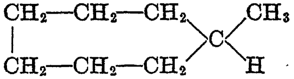


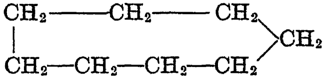
1-cyclopentyl-1-propine (methylcyclopentylacetylene) (278, 280)

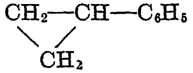
(752) C_8H_{14}

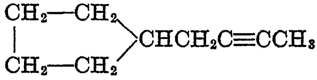


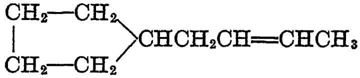
3-cyclopentyl-1-propene (508)

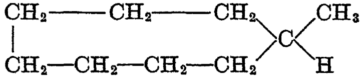
(753) C_8H_{16}  methylcycloheptane (118)

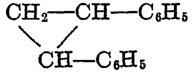
(754) C_8H_{16}  cyclooöctane (118)

(755) C_9H_{10}  phenylcyclopropane (404, 405, 407)

(756) C_9H_{14}  1-cyclopentyl-2-butine (279, 280)

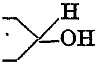
(757) C_9H_{16}  1-cyclopentyl-2-butene (281)

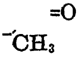
(758) C_9H_{18}  methylcycloöctane (118)

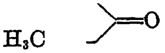
(759) $C_{15}H_{14}$  1,2-diphenylcyclopropane (407)

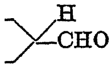
II. Derivatives of cycloparaffins

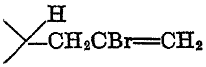
(760) C_5H_8O cyclopentanone (89, 504)

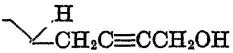
(761) $C_5H_{10}O$  cyclopentanol (505)

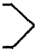
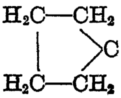
(762) $C_6H_{10}O$  2-methylcyclopentanone (504)

(763) $C_6H_{10}O$  3-methylcyclopentanone (504)

(764) $C_6H_{10}O$  cyclopentanealdehyde (506)

(765) $C_8H_{13}Br$  3-cyclopentyl-2-bromo-1-propene (280, 508)

(766) $C_9H_{14}O$  4-cyclopentyl-2-butin-1-ol (279, 280)

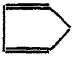
 represents 

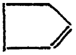
(767) $C_{10}H_{16}O$ ∠$CH_2C{\equiv}CCHOHCH_3$ 5-cyclopentyl-3-pentin-2-ol (279, 280)

(768) $C_{10}H_{16}O$ ∠$CH_2C{\equiv}CCH_2OCH_3$ 1-methoxy-4-cyclopentyl-2-butine (279, 280)

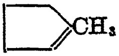
(769) $C_{11}H_{18}O$ ∠$CH_2C{\equiv}CCH(OCH_3)CH_3$ 2-methoxy-5-cyclopentyl-3-pentine (279, 280)

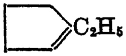
III. *Cycloölefins*

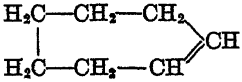
(770) C_5H_6  cyclopentadiene (601)

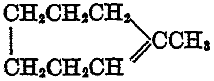
(771) C_5H_8  cyclopentene (69, 260, 505, 508, 636)

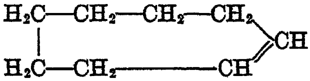
C_6H_{10} (See sections *VII* and *VIII* for cyclohexenes and derivatives)

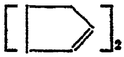
(772) C_6H_{10}  1-methyl-Δ¹-cyclopentene (261, 506, 508)

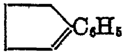
(773) C_7H_{12}  1-ethyl-Δ¹-cyclopentene (261, 506)

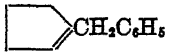
(774) C_7H_{12}  cycloheptene (suberene) (260)

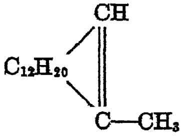
(775) C_8H_{14}  1-methyl-Δ¹-cycloheptene (261)

(776) C_8H_{14}  cycloöctene (260)

(777) $C_{10}H_{12}$  dicyclopentadiene (601)

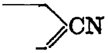
(778) $C_{11}H_{12}$  1-phenyl-Δ¹-cyclopentene (506)

(779) $C_{11}H_{14}$  1-benzyl-Δ¹-cyclopentene (507, 508)

(780) $C_{15}H_{24}$  cedrene (423)

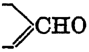
IV. Derivatives of cycloölefins

(781) C_6H_7N



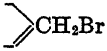
1-cyano-Δ^1-cyclopentene (505, 508)

(782) C_6H_8O



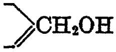
cyclopentenealdehyde (506, 508)

(783) C_6H_9Br



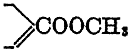
1-bromomethyl-Δ^1-cyclopentene (507)

(784) $C_6H_{10}O$



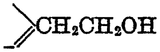
Δ^1-cyclopentenylcarbinol (505, 508)

(785) $C_7H_{10}O_2$



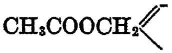
methyl Δ^1-cyclopentenecarboxylate (506, 508)

(786) $C_7H_{12}O$



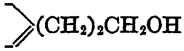
Δ^1-cyclopentenylethanol (505, 508)

(787) $C_8H_{12}O_2$



Δ^1-cyclopentenylcarbinol acetate (507)

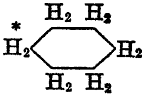
(788) $C_8H_{14}O$



Δ^1-cyclopentenylpropanol (505, 508)

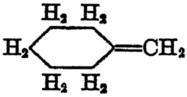
V. Cyclohexanes

(789) C_6H_{12}



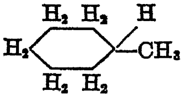
cyclohexane (6, 7, 41, 54, 117, 118, 194, 242, 259, 260, 290, 381, 404, 472, 498, 534, 564, 573, 606, 634, 635, 636, 661)

(790) C_7H_{12}



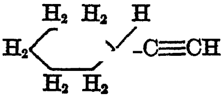
methylenecyclohexane (302)

(791) C_7H_{14}



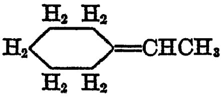
methylcyclohexane (6, 7, 118, 259, 472)

(792) C_8H_{12}

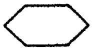
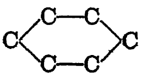


cyclohexylacetylene (278)

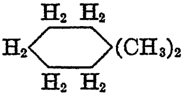
(793) C_8H_{14}



ethylidenecyclohexane (302)

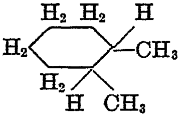
*  represents 

(794) C_8H_{16}



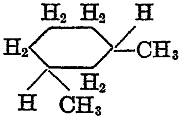
1,1-dimethylcyclohexane (441)

(795) C_8H_{16}



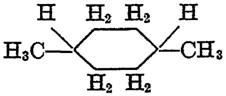
1,2-dimethylcyclohexane (*cis* or *trans*) (259, 402, 439, 440)

(796) C_8H_{16}



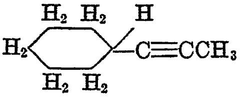
1,3-dimethylcyclohexane (*cis* or *trans*) (6, 7, 259, 441, 472)

(797) C_8H_{16}



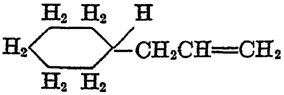
1,4-dimethylcyclohexane (*cis* or *trans*) (6, 7, 259, 441)

(798) C_9H_{14}



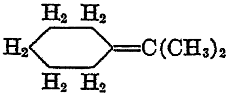
methylcyclohexylacetylene (1-cyclohexyl-1-propine) (278, 280)

(799) C_9H_{16}



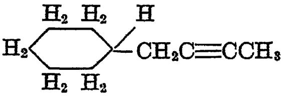
3-cyclohexyl-1-propene (508)

(800) C_9H_{16}



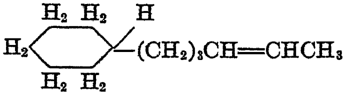
isopropylidenecyclohexane (302)

(801) $C_{10}H_{16}$



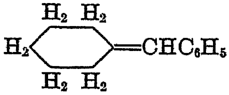
1-cyclohexyl-2-butine (278, 280)

(802) $C_{12}H_{22}$



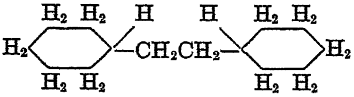
6-cyclohexyl-2-hexene (281)

(803) $C_{13}H_{16}$



benzalcyclohexane (517)

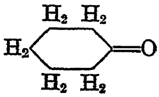
(804) $C_{14}H_{26}$



1,2-dicyclohexylethane (89)

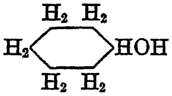
VI. Derivatives of cyclohexane

(805) $C_6H_{10}O$



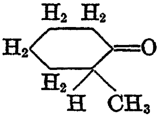
cyclohexanone (208, 472, 504)

(806) $C_6H_{12}O$



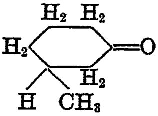
cyclohexanol (456, 472, 498)

(807) $C_7H_{12}O$



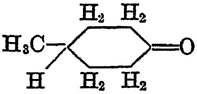
2-methylcyclohexanone (472, 504)

(808) $C_7H_{12}O$



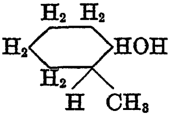
3-methylcyclohexanone (472, 504)

(809) $C_7H_{12}O$



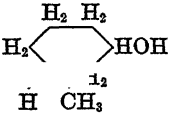
4-methylcyclohexanone (472, 504)

(810) $C_7H_{14}O$



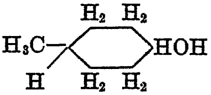
2-methylcyclohexanol (472)

(811) $C_7H_{14}O$



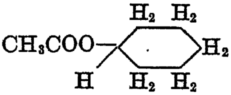
3-methylcyclohexanol (472)

(812) $C_7H_{14}O$



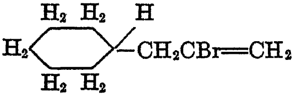
4-methylcyclohexanol (472)

(813) $C_8H_{14}O_2$



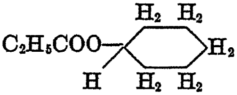
cyclohexyl acetate (472)

(814) $C_9H_{15}Br$



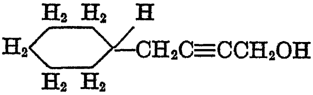
3-cyclohexyl-2-bromo-1-propene (508)

(815) $C_9H_{16}O_2$



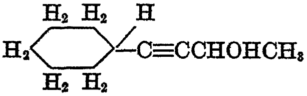
cyclohexyl propionate (472)

(816) $C_{10}H_{16}O$



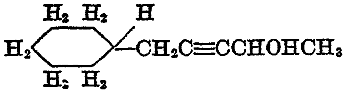
4-cyclohexyl-2-butin-1-ol (276, 280)

(817) $C_{10}H_{16}O$



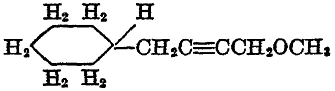
1-cyclohexyl-1-butin 3-ol (278, 280)

(818) $C_{11}H_{18}O$



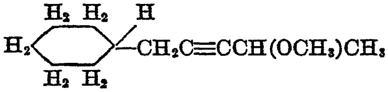
5-cyclohexyl-3-pentin-2-ol (276, 280)

(819) $C_{11}H_{18}O$



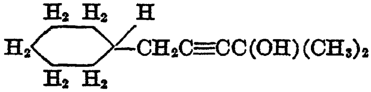
1-cyclohexyl-4-methoxy-2-butine (277, 280)

(820) $C_{12}H_{20}O$



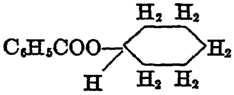
1-cyclohexyl-4-methoxy-2-pentine (277, 280)

(821) $C_{12}H_{20}O$



5-cyclohexyl-2-methyl-3-pentin-2-ol (280)

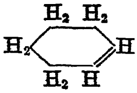
(822) $C_{13}H_{16}O_2$



cyclohexyl benzoate (420)

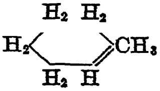
VII. Cyclohexenes

(823) C_6H_{10}



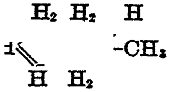
cyclohexene (6, 7, 8, 260, 404, 405, 456, 472, 634, 635, 636, 661)

(824) C_7H_{12}



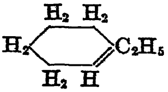
1-methyl-Δ^1-cyclohexene (261)

(825) C_7H_{12}



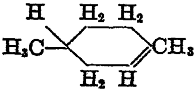
1-methyl-Δ^3-cyclohexene (261)

(826) C_8H_{14}



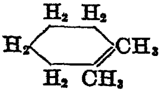
1-ethyl-Δ^1-cyclohexene (261)

(827) C_8H_{14}



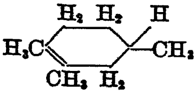
1,4-dimethyl-Δ^1-cyclohexene (261)

(828) C_8H_{14}



1,2-dimethyl-Δ^1-cyclohexene (302)

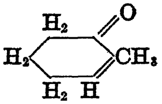
C_9H_{16}



1,3,4-trimethyl-Δ^3-cyclohexene (261)

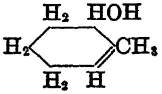
VIII. *Derivatives of cyclohexenes*

(830) $C_7H_{10}O$



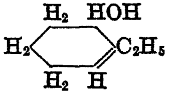
1-methyl-Δ¹-cyclohexen-6-one (508)

(831) $C_7H_{12}O$



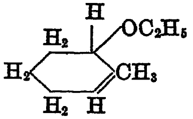
1-methyl-Δ¹-cyclohexen-6-ol (508)

(832) $C_8H_{14}O$



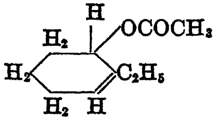
1-ethyl-Δ¹-cyclohexen-6-ol (288)

(833) $C_9H_{16}O$



1-methyl-6-ethoxy-Δ¹-cyclohexene (508)

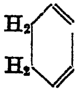
(834) $C_{10}H_{16}O_2$



1-ethyl-Δ¹-cyclohexen-6-ol acetate (288)

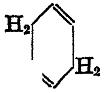
IX. *Cyclohexadienes*

(835) C_6H_8



1,3-cyclohexadiene (8, 90, 92, 370, 461)

(836) C_6H_8



1,4-cyclohexadiene (8, 370)

X. *Terpenes, polycyclic terpenes, and terpene derivatives*

a. Terpenes and terpenoids

(837) $C_{10}H_{14}$

p-cymene (215, 216, 217, 218, 456)

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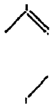
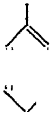
* is the cyclohexane ring. In the unsaturated derivatives, the unsaturation is indicated by double bonds. A single bond extending from the ring represents a CH_3 group, while a $=CH_2$ is indicated by a double bond attached to the ring. ┴ represents $—CH(CH_3)_2$. ┗ represents $—C(=CH_2)CH_3$. A straight line at the midpoint of which two other lines meet represents $H_3C—\overset{|}{\underset{|}{C}}—CH_3$.

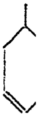


(838) $C_{10}H_{16}$ *dl*-limonene (dipentene) (82, 97, 215, 216, 217, 218, 220, 404, 405, 580)

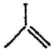


(839) $C_{10}H_{16}$ -phellandrene (215, 216, 217)

(840) $C_{10}H_{16}$ β-phellandrene (215, 216, 217)

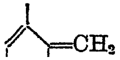


(841) $C_{10}H_{16}$ α-terpinene (218, 220)

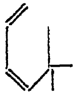


(842) $C_{10}H_{16}$ γ-terpinene (218, 220)

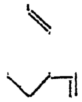
(843) $C_{10}H_{16}$ terpinolene (218, 220)



(844) $C_{10}H_{16}$ α-pyronene (211)



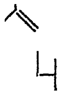
(845) $C_{10}H_{16}$ β-pyronene (211)



(846) $C_{10}H_{16}$ sylvestrene (217)

(847) $C_{10}H_{18}$ Δ³-menthene (76, 82, 218, 404)

(848) $C_{10}H_{18}$ carvomenthene (215, 216, 217, 404, 405)

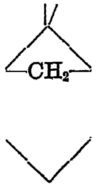


(849) $C_{10}H_{18}$ Δ^1-*m*-menthene (217)

(850) $C_{10}H_{20}$ menthane (82, 215, 216, 217)

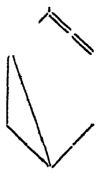
(851) $C_{40}H_{56}$ α- and β-carotene (228)

b. Polycyclic terpenes

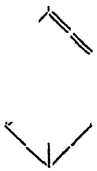


(852) C_9H_{16} nopinane (212, 213, 216)

(853) $C_{10}H_{16}$ sabinene (82, 473)

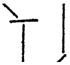


(854) $C_{10}H_{16}$ α-thujene (473)

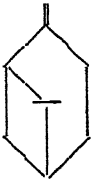


(855) $C_{10}H_{16}$ *dl*-Δ^3-carene (212, 213, 216, 219, 473)

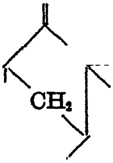
(856) $C_{10}H_{16}$ Δ^4-carene (473)



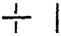
(857) $C_{10}H_{16}$ *dl*-*α*-pinene (56, 76, 80, 82, 199, 212, 213, 216, 219, 328, 473, 598)



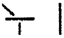
(858) $C_{10}H_{16}$ *β*-pinene (nopinene) (212, 213, 216, 219)



(859) $C_{10}H_{16}$ camphene (212, 213, 216)



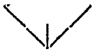
(860) $C_{10}H_{18}$ camphane (212, 213, 216, 218)



(861) $C_{10}H_{18}$ pinane (82, 212, 213, 216)

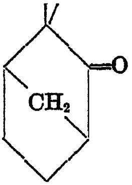
(862) $C_{10}H_{18}$ sabinane (thujane) (82)

(863) $C_{10}H_{18}$ carane (212, 213, 216)

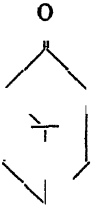


c. Terpene derivatives

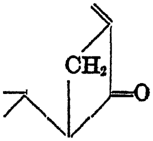
(864) $C_9H_{14}O$ camphenilone (208)



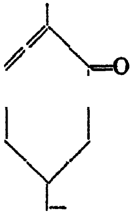
(865) $C_9H_{14}O$ nopinone (208)



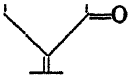
(866) $C_{10}H_{14}O$ verbenone (208)

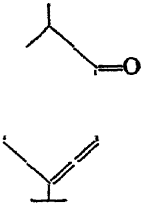


(867) $C_{10}H_{14}O$ carvone (66, 86, 208)

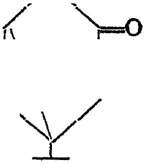


(868) $C_{10}H_{16}O$ pulegone (86, 208)

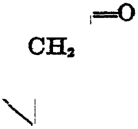




(869) $C_{10}H_{16}O$ carvenone (carveol) (86, 208)



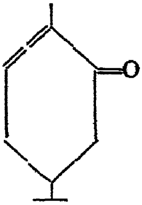
(870) $C_{10}H_{16}O$ β-thujone (86, 208)



(871) $C_{10}H_{16}O$ fenchone (86, 208)

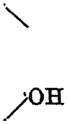
(872) $C_{10}H_{16}O$ camphor (208)

(873) $C_{10}H_{16}O$ dihydrocarvone (208)



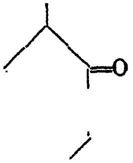
(874) $C_{10}H_{16}O$ carvotanacetone (208)

(875) $C_{10}H_{16}O$ pinocamphone (208)

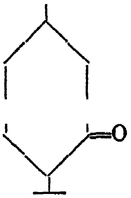


(876) $C_{10}H_{18}O$ isopulegol (66, 67)

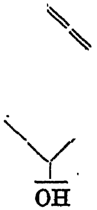
(877) $C_{10}H_{18}O$ dihydrocarvenone (dihydrocarveol) (66, 67)



(878) $C_{10}H_{18}O$ tetrahydrocarvone (66, 208)

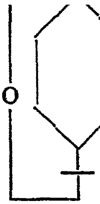


(879) $C_{10}H_{18}O$ menthone (86, 208)



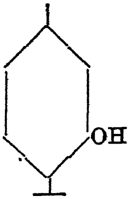
(880) $C_{10}H_{18}O$ α-terpineol (66, 67, 86)

(881) $C_{10}H_{18}O$



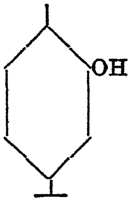
eucalyptol (cineole) (86, 218, 220)

(882) $C_{10}H_{20}O$



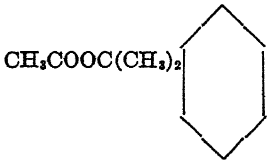
menthol (66, 67)

(883) $C_{10}H_{20}O$



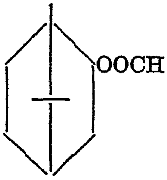
carvomenthol (66, 67)

(884) $C_{10}H_{20}O_2$



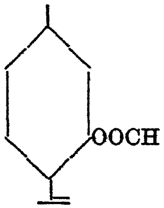
terpenyl acetate (67)

(885) $C_{11}H_{18}O_2$



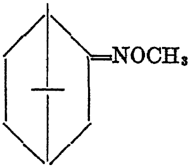
bornyl and isobornyl formate (66, 67)

(886) $C_{11}H_{18}O_2$



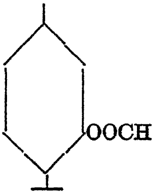
isopulegyl formate (66, 67)

(887) $C_{11}H_{19}NO$



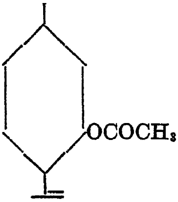
camphor *O*-methyloxime (87, 88)

(888) $C_{11}H_{20}O_2$



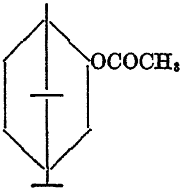
menthyl formate (66, 67)

(889) $C_{12}H_{20}O_2$



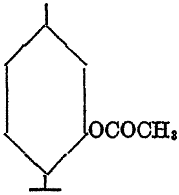
isopulegyl acetate (66, 67)

(890) $C_{12}H_{20}O_2$



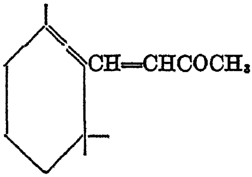
bornyl and isobornyl acetate (66, 67)

(891) $C_{12}H_{22}O_2$



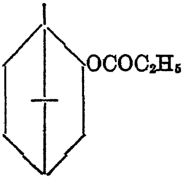
menthyl acetate (66, 67)

(892) $C_{13}H_{20}O$

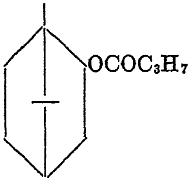


β-ionone (228)

(893) $C_{13}H_{22}O_2$



bornyl and isobornyl propionate (66, 67)

(894) $C_{14}H_{24}O_2$		bornyl and isobornyl butyrate (66 67)
(895) $C_{40}H_{56}O_2$		leaf xanthophyll (228)

B. AROMATIC COMPOUNDS

I. Benzene and monosubstitution derivatives

a. Hydrocarbons

(896) C_6D_6	C_6D_6	benzene-d$_6$ (18, 334, 466, 660)
(897) C_6HD_5	C_6HD_5	benzene-d$_5$ (334)
(898) C_6H_5D	C_6H_5D	benzene-d (18, 334)
(899) C_6H_6	C_6H_6	benzene (6, 7, 23, 24, 27, 28, 40, 41, 42, 48, 51, 54, 55, 58, 61, 70, 108, 109, 112, 113, 117, 119, 121, 122, 129, 136, 137, 139, 141, 143, 153, 155, 156, 157, 158, 159, 161, 170, 192, 194, 196, 201, 204, 221, 226, 227, 235, 236, 237, 242, 247, 271, 286, 291, 292, 293, 321, 322, 334, 381, 394, 415, 433, 434, 435, 438, 452, 459, 465, 475, 512, 515, 519, 523, 524, 526, 534, 537, 543, 546, 547, 555, 556, 561, 564, 566, 572, 573, 575, 576, 577, 578, 579, 587, 624, 625, 634, 635, 636, 639, 640, 641, 647, 648, 650, 654, 655, 657, 658, 659, 660, 661; also 272)
(900) C_7H_8	$C_6H_5CH_3$	toluene (6, 7, 117, 136, 137, 139, 141, 156, 157, 158, 192, 194, 196, 237, 242, 291, 292, 293, 321, 322, 355, 394, 396, 435, 475, 500, 519, 523, 526, 543, 561, 578, 587, 624, 659)
(901) C_8H_6	$C_6H_5C{\equiv}CH$	phenylacetylene (100, 102, 103)
(902) C_8H_8	$C_6H_5CH{=}CH_2$	phenylethylene (styrene) (99, 100, 404, 405, 559)
(903) $(C_8H_8)_x$	$(C_8H_8)_x$	polystyrene (559)
(904) C_8H_{10}	$C_6H_5CH_2CH_3$	ethylbenzene (6, 7, 155, 161, 242, 292, 559)
(905) C_9H_8	$C_6H_5C{\equiv}CCH_3$	methylphenylacetylene (100, 102, 103, 274, 280)
(906) C_9H_8	$C_6H_5CH_2C{\equiv}CH$	benzylacetylene (102, 103)
(907) C_9H_{10}	$C_6H_5CH_2CH{=}CH_2$	benzylethylene (3-phenyl-1-propene) (69, 97, 99, 404, 405)
(908) C_9H_{10}	$C_6H_5CH{=}CHCH_3$	isoallylbenzene (1-phenyl-1-propene) (69, 281, 404, 405)
(909) C_9H_{10}	$C_6H_5CH{=}CHCH_3$	isoallylbenzene (*cis*) (100)
(910) C_9H_{10}	$C_6H_5CH{=}CHCH_3$	isoallylbenzene (*trans*) (100)
(911) C_9H_{12}	$C_6H_5C_3H_7$	propylbenzene (6)
(912) $C_{10}H_{10}$	$C_6H_5C{\equiv}CC_2H_5$	ethylphenylacetylene (274)
(913) $C_{10}H_{12}$	$C_6H_5CH{=}C(CH_3)_2$	β,β-dimethylstyrene (2-methyl-1-phenyl-1-propene) (517, 551)

(914)	$C_{10}H_{14}$	$C_6H_5C_4H_9$	butylbenzene (6, 7)
(915)	$C_{11}H_{10}$	$C_6H_5C\equiv CCH_2CH=CH_2$	allylphenylacetylene (97, 99)
(916)	$C_{11}H_{12}$	$C_6H_5C\equiv CC_3H_7$	propylphenylacetylene (274)
(917)	$C_{11}H_{16}$	$C_6H_5C_5H_{11}$	amylbenzene (6)
(918)	$C_{13}H_{12}$	$C_6H_5CH_2C_6H_5$	diphenylmethane (140, 180, 181, 207)
(919)	$C_{14}H_{10}$	$C_6H_5C\equiv CC_6H_5$	tolane (180, 181)
(920)	$C_{14}H_{12}$	$C_6H_5CH=CHC_6H_5$	stilbene (*cis*) (180, 181)
(921)	$C_{14}H_{12}$	$C_6H_5CH=CHC_6H_5$	stilbene (*trans*) (180, 181)
(922)	$C_{14}H_{14}$	$C_6H_5CH_2CH_2C_6H_5$	dibenzyl (180, 181)

b. Halogen derivatives

1. Fluorine derivatives

(923)	C_6H_5F	C_6H_5F	fluorobenzene (138, 265, 355, 463, 464)

2. Chlorine derivatives

(924)	C_6H_5Cl	C_6H_5Cl	chlorobenzene (57, 69, 129, 153, 157, 159, 187, 191, 237, 294, 395, 462, 465, 519, 561, 573, 587, 625, 654)
(925)	$C_7H_5Cl_3$	$C_6H_5CCl_3$	benzotrichloride (168, 171, 500)
(926)	C_7H_7Cl	$C_6H_5CH_2Cl$	benzyl chloride (129, 155, 205, 500)
(927)	C_8H_5Cl	$C_6H_5C\equiv CCl$	1-chloro-2-phenylacetylene (102, 103)

3. Bromine derivatives

(928)	C_6H_5Br	C_6H_5Br	bromobenzene (57, 102, 117, 153, 157, 159, 237, 355, 462, 498, 510, 587, 625, 659)
(929)	C_8H_7Br	$C_6H_5CH=CHBr$	1-bromo-2-phenylethylene (508)
(930)	C_9H_9Br	$C_6H_5CH_2CBr=CH_2$	2-bromo-2-benzylethylene (404, 405)

4. Iodine derivatives

(931)	C_6H_5I	C_6H_5I	iodobenzene (153, 159, 174, 177, 462, 587)

c. Hydroxyl derivatives

(932)	C_6H_6O	C_6H_5OH	phenol (136, 137, 153, 159, 237, 242, 355, 500)
(933)	C_7H_8O	$C_6H_5CH_2OH$	benzyl alcohol (155, 161, 320)
(934)	$C_8H_{10}O$	$C_6H_5CHOHCH_3$	methylphenylcarbinol (421)
(935)	C_9H_8O	$C_6H_5C\equiv CCH_2OH$	3-phenyl-2-propin-1-ol (276, 280)
(936)	$C_{10}H_{10}O$	$C_6H_5C\equiv CCHOHCH_3$	4-phenyl-3-butin-2-ol (276, 280)
(937)	$C_{10}H_{14}O$	$(C_6H_5CH_2)C(CH_3)_2OH$	dimethylbenzylcarbinol (551)
(938)	$C_{13}H_{12}O$	$(C_6H_5)_2CHOH$	diphenylcarbinol (207)

d. Ethers

(939)	C_7H_8O	$C_6H_5OCH_3$	methyl phenyl ether (anisole) (153, 159, 237, 242, 362, 480, 561)
(940)	$C_{10}H_{10}O$	$C_6H_5C\equiv CCH_2OCH_3$	3-methoxy-1-phenyl-1-propine (277, 280)
(941)	$C_{11}H_{12}O$	$C_6H_5C\equiv CCH(OCH_3)CH_3$	3-methoxy-1-phenyl-1-butine (277, 280)
(942)	$C_{12}H_{10}O$	$C_6H_5OC_6H_5$	diphenyl ether (173, 176, 207, 659)
(943)	$C_{12}H_{17}O$	$C_6H_5C\equiv CC(OCH_3)(CH_3)_2$	3-methoxy-3-methyl-1-phenyl-1-butine (280)
(944)	$C_{14}H_{10}O_4$	$C_6H_5CO\cdot O\cdot O\cdot OCC_6H_5$	benzoyl peroxide

e. Carbonyl compounds

1. Aldehydes

(945) C_7H_6O	C_6H_5CHO	benzaldehyde (5, 28, 136, 137, 153, 159, 294, 361, 414, 485, 486, 500, 561, 627)
(946) C_8H_8O	$C_6H_5CH_2CHO$	phenylacetaldehyde (90, 361)
(947) C_9H_8O	$C_6H_5CH{=}CHCHO$	cinnamaldehyde (361, 369)
(948) C_9H_8O	$C_6H_5CH{=}CHCHO$	cinnamaldehyde (*trans*) (100)

2. Ketones

(949) C_8H_8O	$C_6H_5COCH_3$	acetophenone (153, 155, 159, 242, 361, 561)
(950) $C_9H_{10}O$	$C_6H_5COC_2H_5$	propiophenone (ethyl phenyl ketone) (361)
(951) $C_9H_{10}O$	$C_6H_5CH_2COCH_3$	methyl benzyl ketone (361)
(952) $C_{10}H_{10}O$	$C_6H_5CH{=}CHCOCH_3$	benzalacetone (359, 361)
(953) $C_{10}H_{10}O$	$CH_3CH{=}CHCOC_6H_5$	ethylideneacetophenone (366)
(954) $C_{10}H_{12}O$	$C_6H_5CH_2COC_2H_5$	ethyl benzyl ketone (361)
(955) $C_{11}H_{12}O_2$	$C_6H_5COCH_2COC_2H_5$	benzoylpropionylmethane (359)
(956) $C_{13}H_{10}O$	$C_6H_5COC_6H_5$	benzophenone (155, 161, 361, 375, 594)
(957) $C_{14}H_{10}O_2$	$C_6H_5COCOC_6H_5$	benzil (358)
(958) $C_{14}H_{12}O$	$C_6H_5CH_2COC_6H_5$	desoxybenzoin (361)
(959) $C_{15}H_{12}O$	$C_6H_5CH{=}CHCOC_6H_5$	benzalacetophenone (361)
(960) $C_{15}H_{12}O$	$C_6H_5COCH_2COC_6H_5$	dibenzoylmethane (359)

3. Acyl halides

(961) C_7H_5BrO	C_6H_5COBr	benzoyl bromide (361)
(962) C_7H_5ClO	C_6H_5COCl	benzoyl chloride (155, 161, 361, 420, 561, 592)
(963) C_8H_7ClO	$C_6H_5COCH_2Cl$	phenacyl chloride (361)
(964) C_8H_7ClO	$C_6H_5CH_2COCl$	phenylacetyl chloride (361)
(965) C_9H_7ClO	$C_6H_5CH{=}CHCOCl$	cinnamoyl chloride (361)

f. Acids

(966) $C_7H_6O_2$	C_6H_5COOH	benzoic acid (163, 167, 168, 170, 171, 352)
(967) C_7H_6OS	C_6H_5COSH	thiobenzoic acid (361)
(968) $C_8H_8O_2$	$C_6H_5CH_2COOH$	phenylacetic acid (361)
(969) $C_9H_6O_2$	$C_6H_5C{\equiv}CCOOH$	phenylpropiolic acid (361)
(970) $C_9H_8O_2$	$C_6H_5CH{=}CHCOOH$	cinnamic acid (361)

g. Anhydrides of acids

(971) $C_{14}H_{10}O_3$	$(C_6H_5CO)_2O$	benzoic anhydride (369)

h. Esters

(972) $C_8H_8O_2$	$C_6H_5COOCH_3$	methyl benzoate (163, 167, 355, 369, 420)
(973) $C_8H_8O_2$	$CH_3COOC_6H_5$	phenyl acetate (420)
(974) $C_9H_9BrO_2$	$C_6H_5CHBrCOOCH_3$	methyl phenylbromoacetate (631)
(975) $C_9H_9ClO_2$	$CH_2ClCOOCH_2C_6H_5$	benzyl chloroacetate (456)
(976) $C_9H_{10}O_2$	$C_6H_5COOC_2H_5$	ethyl benzoate (163, 167, 248, 355, 420)
(977) $C_9H_{10}O_2$	$CH_3COOCH_2C_6H_5$	benzyl acetate (456)

(978)	$C_9H_{10}O_2$	$C_6H_5CH_2COOCH_3$	methyl phenylacetate (361, 421)
(979)	$C_{10}H_{10}O_2$	$C_6H_5CH{=}CHCOOCH_3$	methyl cinnamate (361)
(980)	$C_{10}H_{10}O_3$	$C_6H_5COCOOC_2H_5$	ethyl benzoylformate (359)
(981)	$C_{10}H_{12}O_2$	$C_3H_7COOC_6H_5$	phenyl butyrate (420)
(982)	$C_{10}H_{12}O_2$	$C_6H_5COOC_3H_7$	propyl benzoate (420)
(983)	$C_{10}H_{12}O_2$	$C_6H_5COOCH(CH_3)_2$	isopropyl benzoate (420)
(984)	$C_{10}H_{12}O_2$	$C_6H_5CH_2COOC_2H_5$	ethyl phenylacetate (361, 421)
(985)	$C_{11}H_{10}O_2$	$C_6H_5C{\equiv}CCOOC_2H_5$	ethyl phenylpropiolate (361)
	$C_{11}H_{12}O_2$	$C_6H_5CH{=}CHCOOC_2H_5$	ethyl cinnamate (359, 361, 369, 421)
(987)	$C_{11}H_{12}O_3$	$C_6H_5COCH_2COOC_2H_5$	ethyl benzoylacetate (359)
	$C_{11}H_{14}O_2$	$C_6H_5COOC_4H_9$	butyl benzoate (420)
	$C_{11}H_{14}O_2$	$C_6H_5COOCH_2CH(CH_3)_2$	isobutyl benzoate (420)
(990)	$C_{11}H_{14}O_2$	$C_6H_5CH_2CH_2COOC_2H_5$	ethyl hydrocinnamate (90, 361, 421)
(991)	$C_{12}H_{14}O_2$	$C_6H_5CH{=}CHCOOCH(CH_3)_2$	isopropyl cinnamate (421)
(992)	$C_{12}H_{16}O_2$	$C_6H_5COO(CH_2)_2CH(CH_3)_2$	isoamyl benzoate (420)
(993)	$C_{14}H_{12}O_2$	$C_6H_5COOC_6H_4CH_3$	*o*-tolyl benzoate (420)
(994)	$C_{15}H_{22}O_2$	$C_6H_5COOC_8H_{17}$	octyl benzoate (420)

i. Salts

(995)	$C_7H_5NaO_2$	C_6H_5COONa	sodium benzoate (248)

j. Cyano derivatives

(996)	C_7H_5N	C_6H_5CN	benzonitrile (155, 161, 355, 500, 561)
(997)	C_7H_5NO	C_6H_5NCO	phenyl isocyanate (145, 148)
(998)	C_7H_5NS	C_6H_5NCS	phenyl isothiocyanate (145, 148, 485, 501)
(999)	C_8H_7N	$C_6H_5CH_2CN$	benzyl cyanide (169, 172, 320, 500)

k. Mercaptans and sulfides

(1000)	C_6H_6S	C_6H_5SH	phenyl mercaptan (620)
(1001)	$C_{12}H_{10}S$	$C_6H_5SC_6H_5$	diphenyl sulfide (207)
(1002)	$C_{12}H_{10}S_2$	$C_6H_5SSC_6H_5$	diphenyl disulfide (659)
(1003)	$C_{14}H_{14}S$	$C_6H_5CH_2SCH_2C_6H_5$	dibenzyl sulfide (593)

l. Sulfonic acids

(1004)	$C_6H_5ClSO_2$	$C_6H_5SO_2Cl$	benzenesulfonyl chloride (475)
(1005)	$C_6H_6SO_3$	$C_6H_5SO_2OH$	benzenesulfonic acid (475)

m. Amines, amides, imides, and oximes

(1006)	C_6H_7N	$C_6H_5NH_2$	aniline (74, 117, 153, 159, 173, 176, 239, 485)
(1007)	$C_6H_8N_2$	$C_6H_5NHNH_2$	phenylhydrazine (485)
(1008)	C_7H_7NO	$C_6H_5CH{=}NOH$	benzaldoxime (87, 88)
(1009)	C_7H_7NO	$C_6H_5CONH_2$	benzamide (361)
(1010)	$C_7H_8N_2O_2$	$C_6H_5N(CH_3)NO_2$	methylphenylnitramine (173, 176)
(1011)	C_7H_9N	$C_6H_5CH_2NH_2$	benzylamine (168, 171)
(1012)	C_7H_9N	$C_6H_5NHCH_3$	methylaniline (239)
(1013)	C_8H_8NNaO	$C_6H_5C(CH_3){=}NONa$	acetophenone oxime (Na salt) (87, 88)

(1014)	C_8H_9NO	$C_6H_5NHCOCH_3$	acetanilide (594)
(1015)	C_8H_9NO	$C_6H_5C(CH_3){=}NOH$	acetophenone oxime (87, 88)
(1016)	$C_8H_{11}N$	$C_6H_5N(CH_3)_2$	dimethylaniline (74, 155, 161, 239)
(1017)	$C_{10}H_{15}N$	$C_6H_5N(C_2H_5)_2$	diethylaniline (239)
(1018)	$C_{11}H_{13}NO$	$C_6H_5CH{=}CHCOCON(CH_3)_2$	*N*, *N*-dimethylcinnamide (361)
(1019)	$C_{12}H_{11}N$	$(C_6H_5)_2NH$	diphenylamine (173, 176)
(1020)	$C_{13}H_{11}N$	$C_6H_5N{=}CHC_6H_5$	benzalaniline (84)

n. Nitro derivatives

(1021)	$C_6H_5NO_2$	$C_6H_5NO_2$	nitrobenzene (7, 116, 117, 135, 136, 137, 153, 159, 170, 237, 242, 308, 403, 543, 548, 565, 574, 625, 651)
(1022)	$C_7H_6NNaO_2$	$C_6H_5CH{=}NOONa$	*aci*-phenylnitromethane (Na salt) (151)
(1023)	$C_7H_7NO_2$	$C_6H_5CH_2NO_2$	phenylnitromethane (151)

o. Metallo derivatives

(1024)	$C_{12}H_{10}Hg$	$(C_6H_5)_2Hg$	mercury diphenyl (207)
(1025)	$C_{12}H_{10}Se$	$(C_6H_5)_2Se$	selenium diphenyl (207)

II. Disubstituted derivatives of benzene

a. Hydrocarbons

(1026)	C_8H_{10}	$CH_3C_6H_4CH_3$	xylene (60, 142, 153, 159, 194, 242, 294, 332, 654)
(1027)	C_8H_{10}	$CH_3C_6H_4CH_3$	*o*-xylene (6, 8, 93, 142, 153, 156, 157, 159, 242, 355, 659)
(1028)	C_8H_{10}	$CH_3C_6H_4CH_3$	*m*-xylene (8, 142, 153, 156, 157, 159, 242, 355, 561, 659)
(1029)	C_8H_{10}	$CH_3C_6H_4CH_3$	*p*-xylene (6, 7, 8, 142, 153, 156, 157, 159, 242, 355, 659)
(1030)	$C_{10}H_{10}$	$C_6H_4(CH{=}CH_2)_2$	*o*-divinylbenzene (508)
(1031)	$C_{10}H_{14}$	$C_6H_4(C_2H_5)_2$	diethylbenzene (mixt.) (6)
	$C_{10}H_{14}$		cymene (see terpenes)
(1032)	$C_{12}H_{14}$	$C_6H_4(CH{=}CHCH_3)_2$	*o*-diisoallylbenzene (508)

b. Halogen derivatives

(1033)	C_6H_4BrCl	ClC_6H_4Br	*o*-chlorobromobenzene (367, 368)
(1034)	C_6H_4BrCl	ClC_6H_4Br	*m*-chlorobromobenzene (367, 368)
(1035)	C_6H_4BrCl	ClC_6H_4Br	*p*-chlorobromobenzene (367, 368)
(1036)	$C_6H_4BrNO_2$	$BrC_6H_4NO_2$	*o*-bromonitrobenzene (554)
(1037)	$C_6H_4BrNO_2$	$BrC_6H_4NO_2$	*m*-bromonitrobenzene (554)
(1038)	$C_6H_4BrNO_2$	$BrC_6H_4NO_2$	*p*-bromonitrobenzene (554)
(1039)	$C_6H_4Cl_2$	ClC_6H_4Cl	dichlorobenzene (mixt.) (153, 159, 454)
(1040)	$C_6H_4Cl_2$	ClC_6H_4Cl	*o*-dichlorobenzene (153, 159, 187, 191, 454, 465, 584)
(1041)	$C_6H_4Cl_2$	ClC_6H_4Cl	*m*-dichlorobenzene (163, 167, 187, 191, 454, 465, 584)
(1042)	$C_6H_4Cl_2$	ClC_6H_4Cl	*p*-dichlorobenzene (153, 159, 187, 191, 286, 454, 465, 584)

(1043)	C_6H_4ClF	ClC_6H_4F	*o*-chlorofluorobenzene (367, 368)
(1044)	C_6H_4ClF	ClC_6H_4F	*m*-chlorofluorobenzene (367, 368)
(1045)	C_6H_4ClI	ClC_6H_4I	*o*-chloroiodobenzene (367, 368)
(1046)	C_6H_4ClI	ClC_6H_4I	*m*-chloroiodobenzene (367, 368)
(1047)	C_6H_4ClI	ClC_6H_4I	*p*-chloroiodobenzene (367, 368)
(1048)	$C_6H_4ClNO_2$	$ClC_6H_4NO_2$	*o*-chloronitrobenzene (554)
(1049)	$C_6H_4ClNO_2$	$ClC_6H_4NO_2$	*m*-chloronitrobenzene (554)
(1050)	$C_6H_4ClNO_2$	$ClC_6H_4NO_2$	*p*-chloronitrobenzene (554)
(1051)	C_6H_5ClO	ClC_6H_4OH	*o*-chlorophenol (309, 367, 368, 543)
(1052)	C_6H_5ClO	ClC_6H_4OH	*m*-chlorophenol (367, 368)
(1053)	C_6H_5ClO	ClC_6H_4OH	*p*-chlorophenol (367, 368)
(1054)	C_6H_6ClN	$ClC_6H_4NH_2$	*o*-chloroaniline (367, 368)
(1055)	C_6H_6ClN	$ClC_6H_4NH_2$	*m*-chloroaniline (367, 368)
(1056)	C_6H_6ClN	$ClC_6H_4NH_2$	*p*-chloroaniline (367, 368)
(1057)	C_7H_4ClN	ClC_6H_4CN	*o*-chlorobenzonitrile (367, 368)
(1058)	C_7H_4ClN	ClC_6H_4CN	*m*-chlorobenzonitrile (367, 368)
(1059)	C_7H_4ClN	ClC_6H_4CN	*p*-chlorobenzonitrile (367, 368)
(1060)	C_7H_5ClO	ClC_6H_4CHO	*o*-chlorobenzaldehyde (90)
(1061)	C_7H_5ClO	ClC_6H_4CHO	*m*-chlorobenzaldehyde (90)
(1062)	C_7H_5ClO	ClC_6H_4CHO	*p*-chlorobenzaldehyde (90)
(1063)	C_7H_7Br	$BrC_6H_4CH_3$	*o*-bromotoluene (355)
(1064)	C_7H_7Br	$BrC_6H_4CH_3$	*m*-bromotoluene (355)
(1065)	C_7H_7Br	$BrC_6H_4CH_3$	*p*-bromotoluene (355)
(1066)	C_7H_7F	$FC_6H_4CH_3$	*o*-fluorotoluene (355)
(1067)	C_7H_7F	$FC_6H_4CH_3$	*m*-fluorotoluene (355)
(1068)	C_7H_7F	$FC_6H_4CH_3$	*p*-fluorotoluene (355)
(1069)	C_7H_7I	$IC_6H_4CH_3$	*o*-iodotoluene (355)
(1070)	C_7H_7I	$IC_6H_4CH_3$	*m*-iodotoluene (355)
(1071)	C_7H_7I	$IC_6H_4CH_3$	*p*-iodotoluene (355)
(1072)	C_7H_8Cl	$ClC_6H_4CH_3$	*o*-chlorotoluene (316, 355, 554)
(1073)	C_7H_8Cl	$ClC_6H_4CH_3$	*m*-chlorotoluene (316, 355, 554)
(1074)	C_7H_8Cl	$ClC_6H_4CH_3$	*p*-chlorotoluene (316, 355, 554)
(1075)	$C_8H_8Br_2$	$C_6H_4(CH_2Br)_2$	xylene dibromide (449)
(1076)	$C_9H_9ClO_2$	$ClC_6H_4COOC_2H_5$	ethyl *o*-chlorobenzoate (90)
(1077)	$C_9H_9ClO_2$	$ClC_6H_4COOC_2H_5$	ethyl *m*-chlorobenzoate (90)
(1078)	$C_9H_9ClO_2$	$ClC_6H_4COOC_2H_5$	ethyl *p*-chlorobenzoate (90)
(1079)	$C_9H_9BrO_2$	$BrC_6H_4COOC_2H_5$	ethyl *o*-bromobenzoate (90)
(1080)	$C_9H_9BrO_2$	$BrC_6H_4COOC_2H_5$	ethyl *m*-bromobenzoate (90)
(1081)	$C_9H_9BrO_2$	$BrC_6H_4COOC_2H_5$	ethyl *p*-bromobenzoate (90)
(1082)	$C_9H_9IO_2$	$IC_6H_4COOC_2H_5$	ethyl *o*-iodobenzoate (90)
(1083)	$C_9H_9IO_2$	$IC_6H_4COOC_2H_5$	ethyl *m*-iodobenzoate (90)
(1084)	$C_9H_9IO_2$	$IC_6H_4COOC_2H_5$	ethyl *p*-iodobenzoate (90)

c. Hydroxyl derivatives

(1085)	C_6H_5ClO	ClC_6H_4OH	*o*-chlorophenol (309, 351, 367, 368, 543)
(1086)	C_6H_5ClO	ClC_6H_4OH	*m*-chlorophenol (351, 367, 368)
(1087)	C_6H_5ClO	ClC_6H_4OH	*p*-chlorophenol (351, 367, 368)
(1088)	$C_6H_5O_2$	HOC_6H_4OH	catechol (*o*-dihydroxybenzene) (362)
(1089)	$C_6H_5O_2$	HOC_6H_4OH	resorcinol (*m*-dihydroxybenzene) (298, 354, 362)

(1090)	$C_6H_6O_2$	HOC_6H_4OH	hydroquinone (*p*-dihydroxybenzene) (362)
(1091)	$C_7H_6O_2$	HOC_6H_4CHO	salicylaldehyde (o-hydroxybenzaldehyde) (627)
(1092)	$C_7H_6O_2$	HOC_6H_4CHO	*m*-hydroxybenzaldehyde (90)
(1093)	$C_7H_6O_2$	HOC_6H_4CHO	*p*-hydroxybenzaldehyde (90)
(1094)	C_7H_8O	$CH_3C_6H_4OH$	*o*-cresol (355)
(1095)	C_7H_8O	$CH_3C_6H_4OH$	*m*-cresol (355)
(1096)	C_7H_8O	$CH_3C_6H_4OH$	*p*-cresol (355)
(1097)	$C_8H_8O_3$	$HOC_6H_4COOCH_3$	methyl salicylate (421)
(1098)	$C_9H_{10}O_3$	$HOC_6H_4COOC_2H_5$	ethyl salicylate (421)
(1099)	$C_{13}H_{10}O_3$	$HOC_6H_4COOC_6H_5$	phenyl salicylate (salol) (534, 625, 628)

d. Ethers

(1100)	$C_8H_{10}O$	$CH_3C_6H_4OCH_3$	*o*-cresyl methyl ether (316)
(1101)	$C_8H_{10}O$	$CH_3C_6H_4OCH_3$	*m*-cresyl methyl ether (316)
(1102)	$C_8H_{10}O$	$CH_3C_6H_4OCH_3$	*p*-cresyl methyl ether (316)
(1103)	$C_8H_{10}O_2$	$H_3COC_6H_4OCH_3$	*o*-dimethoxybenzene (veratrole) (362)
(1104)	$C_8H_{10}O_2$	$H_3COC_6H_4OCH_3$	*m*-dimethoxybenzene (362)
(1105)	$C_8H_{10}O_2$	$H_3COC_6H_4OCH_3$	*p*-dimethoxybenzene (362)
(1106)	$C_{10}H_{12}O$	CH_3C $H{=}CHCH_3$	anethole (299, 301)

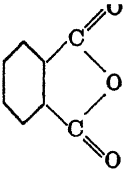
e. Aldehydes

(1107)	C_7H_5ClO	ClC_6H_4CHO	*o*-chlorobenzaldehyde (90)
(1108)	C_7H_5ClO	ClC_6H_4CHO	*m*-chlorobenzaldehyde (90)
(1109)	C_7H_5ClO	ClC_6H_4CHO	*p*-chlorobenzaldehyde (90)
(1110)	$C_7H_5NO_3$	$NO_2C_6H_4CHO$	*o*-nitrobenzaldehyde (151)
(1111)	$C_7H_5NO_3$	$NO_2C_6H_4CHO$	*m*-nitrobenzaldehyde (151)
(1112)	$C_7H_5NO_3$	$NO_2C_6H_4CHO$	*p*-nitrobenzaldehyde (151)
(1113)	$C_7H_6O_2$	HOC_6H_4CHO	salicylaldehyde (*o*-hydroxybenzaldehyde) (627)
(1114)	$C_7H_6O_2$	HOC_6H_4CHO	*m*-hydroxybenzaldehyde (90)
(1115)	$C_7H_6O_2$	HOC_6H_4CHO	*p*-hydroxybenzaldehyde (90)
(1116)	C_8H_8O	$CH_3C_6H_4CHO$	*o*-tolualdehyde (90)
(1117)	C_8H_8O	$CH_3C_6H_4CHO$	*m*-tolualdehyde (90)
(1118)	C_8H_8O	$CH_3C_6H_4CHO$	*p*-tolualdehyde (90)
(1119)	$C_8H_8O_2$	$CH_3OC_6H_4CHO$	*p*-anisaldehyde (627)
(1120)	$C_{10}H_{12}O$	$(CH_3)_2CHC_6H_4CHO$	cuminaldehyde (90)

f. Acids

(1121)	$C_7H_5NO_4$	$NO_2C_6H_4COOH$	*o*-nitrobenzoic acid (69, 151)
(1122)	$C_7H_5NO_4$	$NO_2C_6H_4COOH$	*m*-nitrobenzoic acid (69, 151)
(1123)	$C_7H_5NO_4$	$NO_2C_6H_4COOH$	*p*-nitrobenzoic acid (69, 151)

g. Anhydrides of acids

(1124)	$C_8H_4O_3$		phthalic anhydride (369)

h. Esters

(1125)	$C_8H_8O_3$	$HOC_6H_4COOCH_3$	methyl salicylate (421)
(1126)	$C_9H_9BrO_2$	$BrC_6H_4COOC_2H_5$	ethyl *o*-bromobenzoate (90)
(1127)	$C_9H_9BrO_2$	$BrC_6H_4COOC_2H_5$	ethyl *m*-bromobenzoate (90)
(1128)	$C_9H_9BrO_2$	$BrC_6H_4COOC_2H_5$	ethyl *p*-bromobenzoate (90)
(1129)	$C_9H_9IO_2$	$IC_6H_4COOC_2H_5$	ethyl *o*-iodobenzoate (90)
(1130)	$C_9H_9IO_2$	$IC_6H_3COOC_2H_5$	ethyl *m*-iodobenzoate (90)
(1131)	$C_9H_9IO_2$	$IC_6H_4COOC_2H_5$	ethyl *p*-iodobenzoate (90)
(1132)	$C_9H_9ClO_2$	$ClC_6H_4COOC_2H_5$	ethyl *o*-chlorobenzoate (90)
(1133)	$C_9H_9ClO_2$	$ClC_6H_4COOC_2H_5$	ethyl *m*-chlorobenzoate (90)
(1134)	$C_9H_9ClO_2$	$ClC_6H_4COOC_2H_5$	ethyl *p*-chlorobenzoate (90)
(1135)	$C_9H_{10}O_2$	$CH_3C_6H_4COOCH_3$	methyl *o*-toluate (355, 420)
(1136)	$C_9H_{10}O_2$	$CH_3C_6H_4COOCH_3$	methyl *m*-toluate (355)
(1137)	$C_9H_{10}O_2$	$CH_3C_6H_4COOCH_3$	methyl *p*-toluate (355)
(1138)	$C_9H_{10}O_3$	$HOC_6H_4COOC_2H_5$	ethyl salicylate (421)
(1139)	$C_{10}H_{10}O_4$	$CH_3OOCC_6H_4COOCH_3$	dimethyl phthalate (369, 421)
(1140)	$C_{10}H_{12}O_2$	$CH_3C_6H_4COOC_2H_5$	ethyl *o*-toluate (355)
(1141)	$C_{10}H_{12}O_2$	$CH_3C_6H_4COOC_2H_5$	ethyl *m*-toluate (355)
(1142)	$C_{10}H_{12}O_2$	$CH_3C_6H_4COOC_2H_5$	ethyl *p*-toluate (355)
(1143)	$C_{12}H_{14}O_4$	$C_6H_4(COOC_2H_5)_2$	diethyl phthalate (369, 421)
(1144)	$C_{12}H_{14}O_4$	$H_5C_2OOCC_6H_4COOC_2H_5$	diethyl isophthalate (90)
(1145)	$C_{12}H_{14}O_4$	$H_5C_2OOCC_6H_4COOC_2H_5$	diethyl terephthalate (90)
(1146)	$C_{13}H_{10}O_3$	$HOC_6H_4COOC_6H_5$	phenyl salicylate (534, 625, 628)
(1147)	$C_{14}H_{12}O_2$	$C_6H_5COOC_6H_4CH_3$	*o*-tolyl benzoate (420)

i. Cyano derivatives

(1148)	C_7H_4ClN	ClC_6H_4CN	*o*-chlorobenzonitrile (351, 367, 368)
(1149)	C_7H_4ClN	ClC_6H_4CN	*m*-chlorobenzonitrile (351, 367, 368)
(1150)	C_7H_4ClN	ClC_6H_4CN	*p*-chlorobenzonitrile (351, 367, 368)
(1151)	C_8H_7N	$CH_3C_6H_4CN$	*o*-tolunitrile (145, 148, 355)
(1152)	C_8H_7N	$CH_3C_6H_4CN$	*m*-tolunitrile (355)
(1153)	C_8H_7N	$CH_3C_6H_4CN$	*p*-tolunitrile (355)
(1154)	C_8H_7NS	$CH_3C_6H_4NCS$	*p*-tolyl isothiocyanate (145, 148)

j. Sulfonic acids

(1155)	$C_7H_8\ SO_3$	$CH_3C_6H_4SO_2OH$	toluene-*p*-sulfonic acid (475)

k. Amines and oximes

(1156)	C_6H_6ClN	$ClC_6H_4NH_2$	*o*-chloroaniline (351, 367, 368)
(1157)	C_6H_6ClN	$ClC_6H_4NH_2$	*m*-chloroaniline (351, 367, 368)

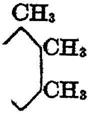
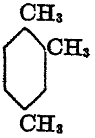
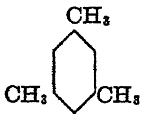
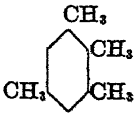
(1158)	C_6H_6ClN	$ClC_6H_4NH_2$	*p*-chloroaniline (351, 367, 368)
(1159)	C_7H_5ClNO	$ClC_6H_5CH{=}NOH$	*o*-chlorobenzaldoxime (87, 88)
(1160)	C_7H_9N	$CH_3C_6H_4NH_2$	*o*-toluidine (239, 355, 454)
(1161)	C_7H_9N	$CH_3C_6H_4NH_2$	*m*-toluidine (239, 355, 454)
(1162)	C_7H_9N	$CH_3C_6H_4NH_2$	*p*-toluidine (239, 355, 454)
(1163)	$C_{13}H_{10}ClN$	$C_6H_5CH{=}NC_6H_4Cl$	benzal *p*-chloroaniline (84)
(1164)	$C_{13}H_{10}ClN$	$ClC_6H_4CH{=}NC_6H_5$	*p*-chlorobenzalaniline (84)
(1165)	$C_{13}H_{11}N$	$C_6H_5N{=}CHC_6H_5$	benzalaniline (84)
(1166)	$C_{14}H_{13}NO$	$C_6H_5CONHC_6H_4CH_3$	benzoyl *p*-toluidine (84)

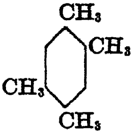
l. Nitro derivatives

(1167)	$C_6H_4BrNO_2$	$BrC_6H_4NO_2$	*o*-bromonitrobenzene (554)
(1168)	$C_6H_4BrNO_2$	$BrC_6H_4NO_2$	*m*-bromonitrobenzene (554)
(1169)	$C_6H_4BrNO_2$	$BrC_6H_4NO_2$	*p*-bromonitrobenzene (554)
(1170)	$C_6H_4ClNO_2$	$ClC_6H_4NO_2$	*o*-chloronitrobenzene (554)
(1171)	$C_6H_4ClNO_2$	$ClC_6H_4NO_2$	*m*-chloronitrobenzene (554)
(1172)	$C_6H_4ClNO_2$	$ClC_6H_4NO_2$	*p*-chloronitrobenzene (554)
(1172A)	$C_7H_5NO_3$	$NO_2C_6H_4CHO$	*o*-nitrobenzaldehyde (151)
(1173)	$C_7H_5NO_3$	$NO_2C_6H_4CHO$	*m*-nitrobenzaldehyde (151)
(1174)	$C_7H_5NO_3$	$NO_2C_6H_4CHO$	*p*-nitrobenzaldehyde (151)
(1175)	$C_7H_5NO_4$	$NO_2C_6H_4COOH$	*o*-nitrobenzoic acid (69, 151)
(1176)	$C_7H_5NO_4$	$NO_2C_6H_4COOH$	*m*-nitrobenzoic acid (69, 151)
(1177)	$C_7H_5NO_4$	$NO_2C_6H_4COOH$	*p*-nitrobenzoic acid (69, 151)
(1178)	$C_7H_7NO_2$	$NO_2C_6H_4CH_3$	nitrotoluene (151, 242, 454, 543)
(1179)	$C_7H_7NO_2$	$NO_2C_6H_4CH_3$	*o*-nitrotoluene (69, 151, 242, 316, 454)
(1180)	$C_7H_7NO_2$	$NO_2C_6H_4CH_3$	*m*-nitrotoluene (69, 151, 242, 316, 454)
(1181)	$C_7H_7NO_2$	$NO_2C_6H_4CH_3$	*p*-nitrotoluene (69, 151, 242, 316, 454)

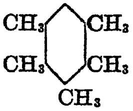
III. Tri-, tetra-, penta-, and hexa-substitution derivatives of benzene

a. Hydrocarbons

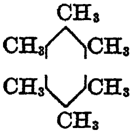
(1182)	C_9H_{12}		1,2,3-trimethylbenzene (362)
(1183)	C_9H_{12}		1,2,4-trimethylbenzene (362)
(1184)	C_9H_{12}		1,3,5-trimethylbenzene (mesitylene) (6, 8, 367, 625, 627)
(1185)	$C_{10}H_{14}$		1,2,3,5-tetramethylbenzene (362)

(1186) $C_{10}H_{14}$


1,2,4,5-tetramethylbenzene (362)

(1187) $C_{11}H_{16}$


pentamethylbenzene (362)

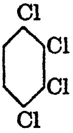
(1188) $C_{12}H_{18}$


hexamethylbenzene (362, 463)

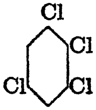
(1189) $C_{12}H_{18}$ $C_6H_3(C_2H_5)_3$ triethylbenzene (mixt.) (6)
(1190) $C_{14}H_{22}$ $C_6H_2(C_2H_5)_4$ tetraethylbenzene (mixt.) (6)

b. Halogen derivatives

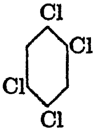
(1191) C_6Cl_6 C_6Cl_6 hexachlorobenzene (187, 191, 463, 465)
(1192) C_6HCl_5 C_6HCl_5 pentachlorobenzene (187, 191, 463)

(1193) $C_6H_2Cl_4$


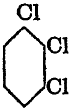
1,2,3,4-tetrachlorobenzene (187, 191)

(1194) $C_6H_2Cl_4$


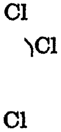
1,2,3,5-tetrachlorobenzene (69, 187, 191)

(1195) $C_6H_2Cl_4$


1,2,4,5-tetrachlorobenzene (187, 191, 463)

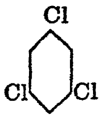
(1196) $C_6H_3Cl_3$


1,2,3-trichlorobenzene (187, 191, 465)

(1197) $C_6H_3Cl_3$


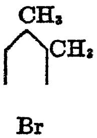
1,2,4-trichlorobenzene (187, 191, 456, 463, 465)

(1198) $C_6H_3Cl_3$



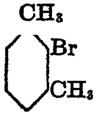
1,3,5-trichlorobenzene (187, 191, 465)

(1199) C_8H_9Br



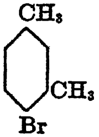
1,2-dimethyl-4-bromobenzene (360)

(1200) C_8H_9Br



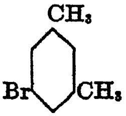
1,3-dimethyl-2-bromobenzene (360)

(1201) C_8H_9Br



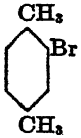
1,3-dimethyl-4-bromobenzene (360)

(1202) C_8H_9Br



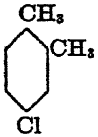
1,3-dimethyl-5-bromobenzene (360)

(1203) C_8H_9Br



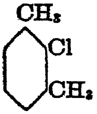
1,4-dimethyl-2-bromobenzene (360)

(1204) C_8H_9Cl



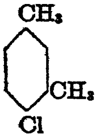
1,2-dimethyl-4-chlorobenzene (360)

(1205) C_8H_9Cl



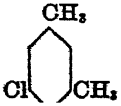
1,3-dimethyl-2-chlorobenzene (360)

(1206) C_8H_9Cl

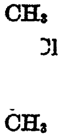


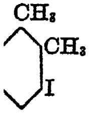
1,3-dimethyl-4-chlorobenzene (360)

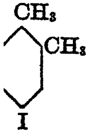
(1207) C_8H_9Cl

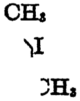


1,3-dimethyl-5-chlorobenzene (360)

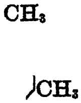
(1208) C_8H_9Cl  1,4-dimethyl-2-chlorobenzene (360)

(1209) C_8H_9I  1,2-dimethyl-3-iodobenzene (360)

(1210) C_8H_9I  1,2-dimethyl-4-iodobenzene (360)

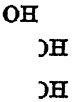
(1211) C_8H_9I  1,3-dimethyl-2-iodobenzene (360)

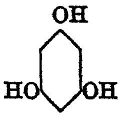
(1212) C_8H_9I 1,3-dimethyl-4-iodobenzene (360)

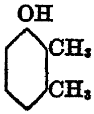
(1213) C_8H_9I  1,3-dimethyl-5-iodobenzene (360)

(1214) C_8H_9I 1,4-dimethyl-2-iodobenzene (360)

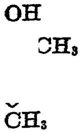
c. Hydroxyl derivatives

(1215) $C_6H_6O_3$  pyrogallol (362)

(1216) $C_6H_6O_3$  phloroglucinol (362)

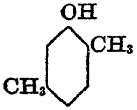
(1217) $C_8H_{10}O$  1,2,3-xylenol (184, 188)

(1218) $C_8H_{10}O$



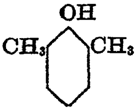
1,2,4-xylenol (184, 188)

(1219) $C_8H_{10}O$



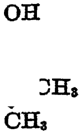
1,2,5-xylenol (184, 188)

(1220) $C_8H_{10}O$



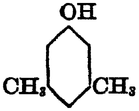
1,2,6-xylenol (184, 188)

(1221) $C_8H_{10}O$



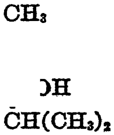
1,3,4-xylenol (184, 188)

(1222) $C_8H_{10}O$



1,3,5-xylenol (184, 188)

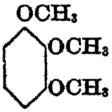
(1223) $C_{10}H_{14}O$



thymol (628)

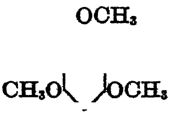
d. Ethers

(1224) $C_9H_{12}O_3$



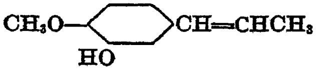
1,2,3-trimethoxybenzene (362)

(1225) $C_9H_{12}O_3$



1,3,5-trimethoxybenzene (362)

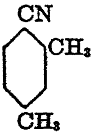
(1226) $C_{10}H_{12}O_2$



isoeugenol (300, 301)

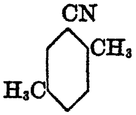
e. Cyano derivatives

(1227) C_9H_9N



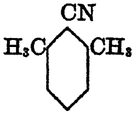
2,4-dimethylbenzonitrile (360)

(1228) C_9H_9N



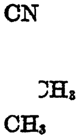
2,5-dimethylbenzonitrile (360)

(1229) C_9H_9N



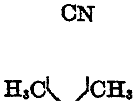
2,6-dimethylbenzonitrile (360)

(1230) C_9H_9N



3,4-dimethylbenzonitrile (360)

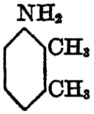
(1231) C_9H_9N



3,5-dimethylbenzonitrile (360)

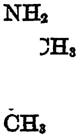
f. Amino derivatives

(1232) $C_8H_{11}N$



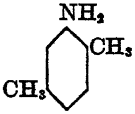
1,2,3-xylidine (184, 188)

(1233) $C_8H_{11}N$



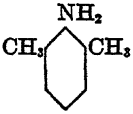
1,2,4-xylidine (184, 188)

(1234) $C_8H_{11}N$



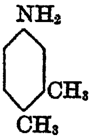
1,2,5-xylidine (184, 188)

(1235) $C_8H_{11}N$



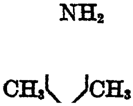
1,2,6-xylidine (184, 188, 239)

(1236) $C_8H_{11}N$



1,3,4-xylidine (184, 188)

(1237) $C_8H_{11}N$



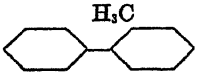
1,3,5-xylidine (184, 188, 239)

IV. Diphenyl and derivatives of diphenyl

a. Hydrocarbons

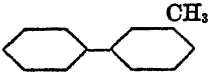
(1238) $C_{12}H_{10}$ diphenyl (163, 167, 207, 658, 659)

(1239) $C_{13}H_{12}$



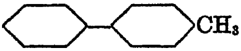
2-methyldiphenyl (89)

(1240) $C_{13}H_{12}$



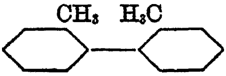
3-methyldiphenyl (89)

(1241) $C_{13}H_{12}$



4-methyldiphenyl (89)

(1242) $C_{14}H_{14}$



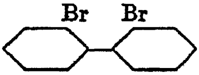
2,2′-dimethyldiphenyl (89)

H_3C CH_3

(1243) $C_{14}H_{14}$ 3,3′-dimethyldiphenyl (89)

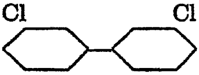
b. Halogen derivatives

(1244) $C_{12}H_8Br_2$



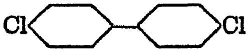
2,2′-dibromodiphenyl (90)

(1245) $C_{12}H_8Cl_2$



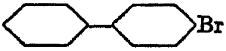
3,3′-dichlorodiphenyl (89)

(1246) $C_{12}H_8Cl_2$



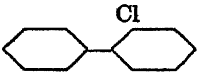
4,4′-dichlorodiphenyl (89)

(1247) $C_{12}H_9Br$



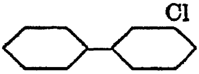
4-bromodiphenyl (89)

(1248) $C_{12}H_9Cl$



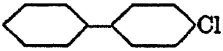
2-chlorodiphenyl (89)

(1249) $C_{12}H_9Cl$



3-chlorodiphenyl (89)

(1250) $C_{12}H_9Cl$



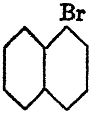
4-chlorodiphenyl (89)

V. Polycyclic compounds

(1251) C_9H_8

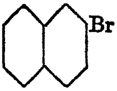
indene (89, 258, 299)

(1252) $C_{10}H_7Br$



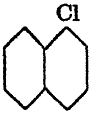
1-bromonaphthalene (258, 671)

(1253) $C_{10}H_7Br$



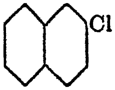
2-bromonaphthalene (174, 177, 258)

(1254) $C_{10}H_7Cl$



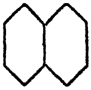
1-chloronaphthalene (258, 671)

(1255) $C_{10}H_7Cl$



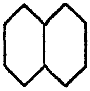
2-chloronaphthalene (258, 671)

(1256) $C_{10}H_7F$



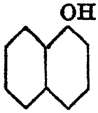
1-fluoronaphthalene (258)

(1257) $C_{10}H_8$



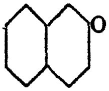
naphthalene (22, 153, 159, 258, 287, 343, 438, 498, 671)

(1258) $C_{10}H_8O$



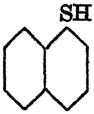
1-naphthol (258)

(1259) $C_{10}H_8O$



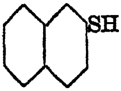
2-naphthol (258)

(1260) $C_{10}H_8S$



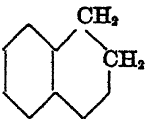
1-naphthyl mercaptan (258)

(1261) $C_{10}H_8S$



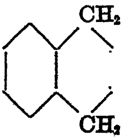
2-naphthyl mercaptan (258)

(1262) $C_{10}H_{10}$



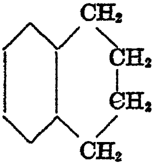
1,2-dihydronaphthalene (69, 299)

(1263) $C_{10}H_{10}$



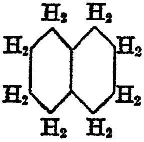
1,4-dihydronaphthalene (69, 85, 299)

(1264) $C_{10}H_{12}$



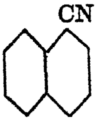
1,2,3,4-tetrahydronaphthalene (81, 457, 458)

(1265) $C_{10}H_{18}$



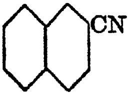
decahydronaphthalene (81, 457, 458)

(1266) $C_{11}H_7N$



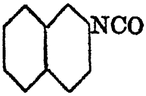
1-naphthyl cyanide (258)

(1267) $C_{11}H_7N$



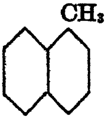
2-naphthyl cyanide (258)

(1268) $C_{11}H_7NO$



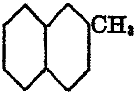
2-naphthyl isocyanate (145, 148)

(1269) $C_{11}H_{10}$



1-methylnaphthalene (258, 671)

(1270) $C_{11}H_{10}$



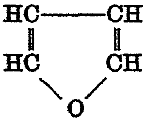
2-methylnaphthalene (258, 671)

C. HETEROCYCLIC COMPOUNDS

I. Monocyclic compounds

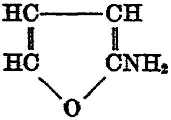
a. Compounds containing ring oxygen

(1271) C_4H_4O



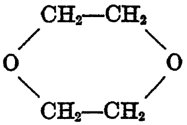
furan (69, 70, 91, 257, 426, 517)

(1272) C_4H_5NO



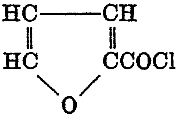
2-furylamine (69, 91)

(1273) $C_4H_8O_2$



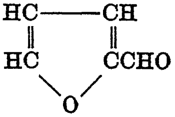
dioxane (630, 652)

(1274) $C_5H_3ClO_2$



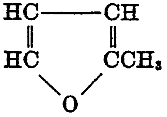
2-furoyl chloride (422)

(1275) $C_5H_4O_2$



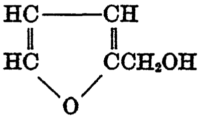
2-furaldehyde (furfural) (91, 257, 369, 414, 422, 426)

(1276) C_5H_6O



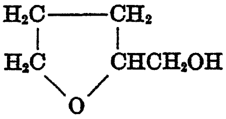
2-methylfuran (422, 426)

(1277) $C_5H_6O_2$



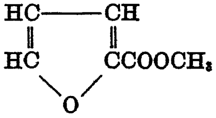
2-furylcarbinol (69, 422, 426, 517)

(1278) $C_5H_{10}O_2$



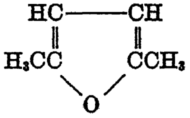
tetrahydro-2-furylcarbinol (422)

(1279) $C_6H_6O_3$



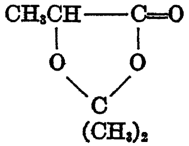
methyl 2-furoate (methyl pyromucate) (422)

(1280) C_6H_8O



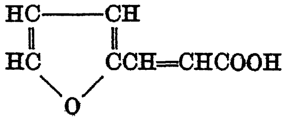
2,5-dimethylfuran (69, 91)

(1281) $C_6H_{10}O_3$



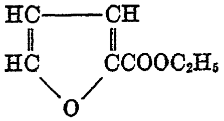
acetone lactic acid (479)

(1282) $C_7H_6O_3$



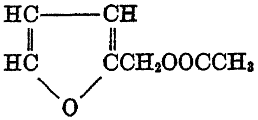
2-furylacrylic acid (422)

(1283) $C_7H_8O_3$



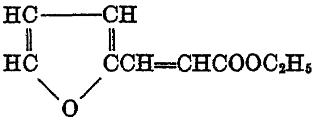
ethyl 2-furoate (ethyl pyromucate) (91, 422)

(1284) $C_7H_8O_3$



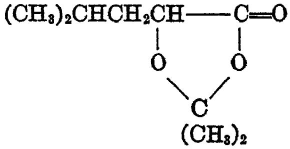
2-furylcarbinol acetate (422)

(1285) $C_9H_{10}O_3$



ethyl 2-furylacrylate (422)

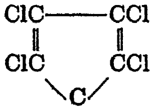
(1286) $C_9H_{16}O_3$



acetone leuicic acid (479)

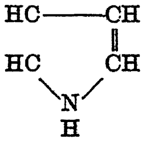
b. Compounds containing ring nitrogen

(1287) C_4HCl_4N



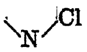
tetrachloropyrrole (96)

(1288) C_4H_5N



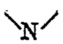
pyrrole (69, 70, 91, 95, 619, 625)

(1289) C_5H_4ClN



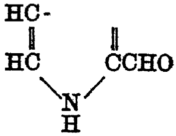
2-chloropyridine (462)

(1290) C_5H_5N



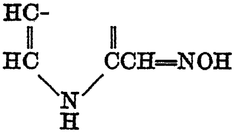
pyridine (75, 129, 242, 359, 378, 379, 480, 498, 621, 625, 645)

(1291) C_5H_5NO



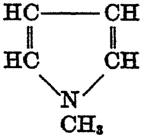
2-pyrrolealdehyde (96)

(1292) C_5H_6NO



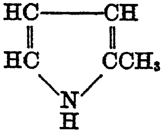
2-pyrrolealdoxime (96)

(1293) C_5H_7N



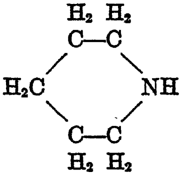
1-methylpyrrole (95, 96)

(1294) C_5H_7N



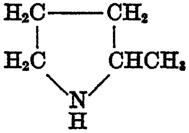
2-methylpyrrole (95)

(1295) $C_5H_{11}N$



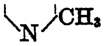
piperidine (73, 75,

(1296) $C_5H_{11}N$



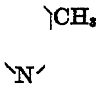
2-methylpyrrolidine (95)

(1297) C_6H_7N



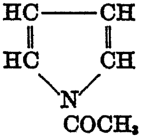
2-methylpyridine (α-picoline) (89, 480)

(1298) C_6H_7N



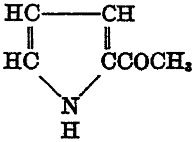
3-methylpyridine (β-picoline) (89)

(1299) C_6H_7NO



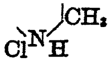
1-acetylpyrrole (95)

(1300) C_6H_7NO



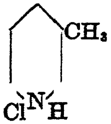
2-acetylpyrrole (96)

(1301) C_6H_8ClN



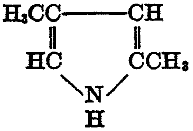
2-methylpyridine hydrochyloride (89)

(1302) C_6H_8ClN



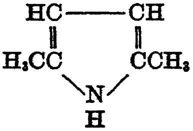
3-methylpyridine hydrochloride (89)

(1303) C_6H_9N



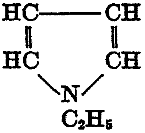
2,4-dimethylpyrrole (96)

(1304) C_6H_9N



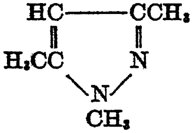
2,5-dimethylpyrrole (96)

(1305) C_6H_9N



1-ethylpyrrole (90)

(1306) $C_6H_{10}N_2$

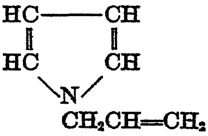


1,3,5-trimethylpyrazole (89)

(1307) $C_6H_{12}N_4$ $C_6H_{12}N_4$ hexamine (hexamethylenetetramine) (376)

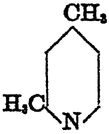
(1308) $C_6H_{13}ClN_4$ $C_6H_{13}ClN_4$ hexamine hydrochloride (377)

(1309) C_7H_9N



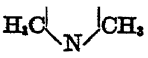
1-allylpyrrole (69, 89)

(1310) C_7H_9N



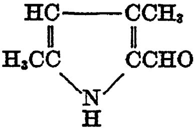
2,4-dimethylpyridine (89)

(1311) C_7H_9N



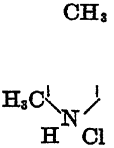
2,6-dimethylpyridine (89)

(1312) C_7H_9NO



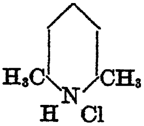
3,5-dimethyl-2-pyrrolealdehyde (96)

(1313) $C_7H_{10}ClN$



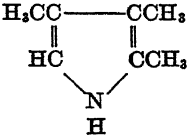
2,4-dimethylpyridine hydrochloride (89)

(1314) $C_7H_{10}ClN$



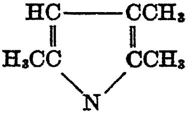
2,6-dimethylpyridine hydrochloride (89)

(1315) $C_7H_{11}N$



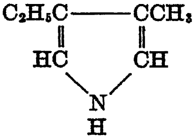
2,3,4-trimethylpyrrole (96)

(1316) $C_7H_{11}N$



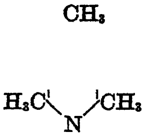
2,3,5-trimethylpyrrole (96)

(1317) $C_7H_{11}N$



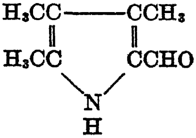
3-methyl-4-ethylpyrrole (opsopyrrole) (95)

(1318) $C_8H_{11}N$



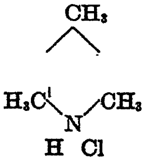
2,4,6-trimethylpyridine (89)

(1319) $C_8H_{11}NO$



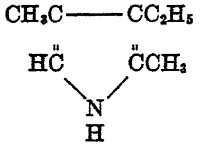
3,4,5-trimethyl-2-pyrrolealdehyde (90)

(1320) $C_8H_{12}ClN$



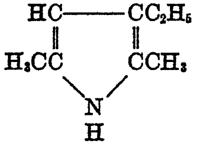
2,4,6-trimethylpyridine hydrochloride (89)

(1321) $C_8H_{13}N$



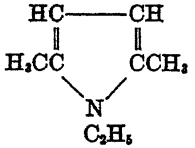
2,4-dimethyl-3-ethylpyrrole (kryptopyrrole) (95)

(1322) $C_8H_{13}N$



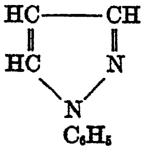
2,5-dimethyl-3-ethylpyrrole (89)

(1323) $C_8H_{13}N$



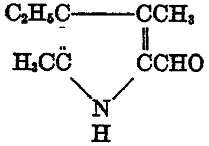
2,5-dimethyl-1-ethylpyrrole (89)

(1324) $C_9H_8N_2$



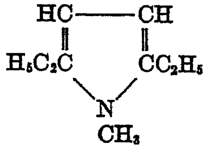
1-phenylpyrazole (89)

(1325) $C_9H_{13}NO$



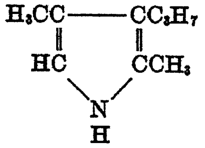
3,5-dimethyl-4-ethyl-2-pyrrole-aldehyde (90)

(1326) $C_9H_{15}N$



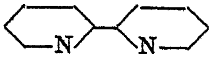
1-methyl-2,5-diethylpyrrole (90)

(1327) $C_9H_{15}N$



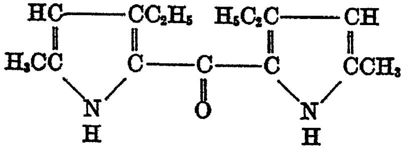
2,4-dimethyl-3-propylpyrrole (95)

(1328) $C_{10}H_8N_2$



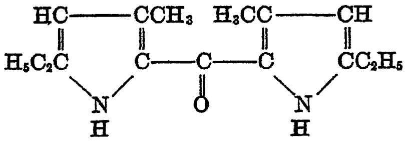
α,α-dipyrridyl (89)

(1329) $C_{15}H_{20}N_2O$



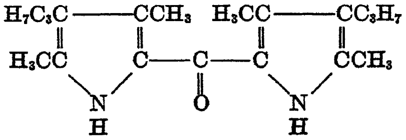
3,3′-diethyl-5,5′-dimethyl-2,2′-dipyrryl ketone (96)

(1330) $C_{15}H_{20}N_2O$



3,3′-dimethyl-5,5′-diethyl-2,2′-dipyrryl ketone (96)

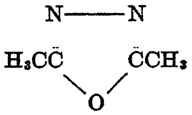
(1331) $C_{19}H_{28}N_2O$



3,3′-dimethyl-5,5′-dimethyl-4,4′-dipropyl-2,2′-dipyrryl ketone (96)

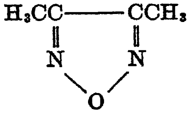
c. Compounds containing ring oxygen and nitrogen

(1332) $C_4H_6N_2O$



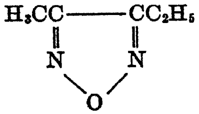
2,5-dimethyloxdiazole (446, 447)

(1333) $C_4H_6N_2O$



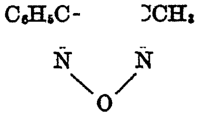
3,4-dimethylfurazan (446, 447)

(1334) $C_5H_8N_2O$



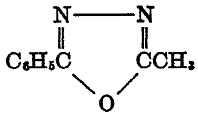
4-methyl-3-ethylfurazan (446, 447)

(1335) $C_9H_8N_2O$



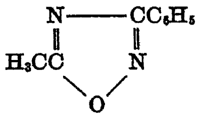
3-methyl-4-phenylfurazan (443)

(1336) $C_9H_8N_2O$



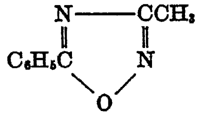
2-methyl-5-phenyloxdiazole (443)

(1337) $C_9H_8N_2O$



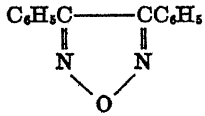
5-methyl-3-phenylazoxime (443)

(1338) $C_9H_8N_2O$



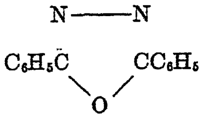
3-methyl-5-phenylazoxime (443)

(1339) $C_{14}H_{10}N_2O$



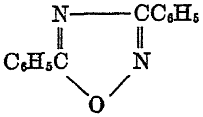
3,4-diphenylfurazan (443)

(1340) $C_{14}H_{10}N_2O$



2,5-diphenyloxdiazole (443)

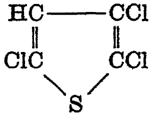
(1341) $C_{14}H_{10}N_2O$



3,5-diphenylazoxime (443)

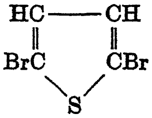
d. Compounds containing ring sulfur

(1342) C_4HCl_3S



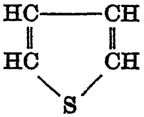
2,3,5-trichlorothiophene (91)

(1343) $C_4H_2Br_2S$



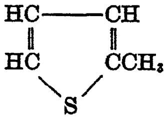
2,5-dibromothiophene (91)

(1344) C_4H_4S



thiophene (48, 61, 69, 91, 94, 619, 625, 628)

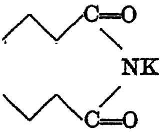
(1345) C_5H_6S



2-methylthiophene (91)

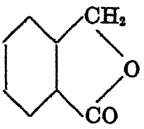
II. Polycyclic compounds

(1346) $C_8H_4KNO_2$



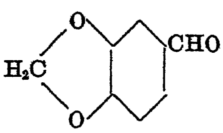
potassium phthalimide (369)

(1347) $C_8H_6O_2$



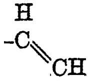
phthalide (369)

(1348) $C_8H_6O_3$



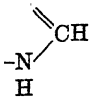
piperonal (90)

(1349) C_8H_6S



thionaphthene (90)

(1350) C_8H_7N



indole (90, 93)

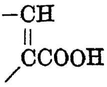
(1351) C_9H_7N

quinoline (83, 89, 242)

(1352) C_9H_7N

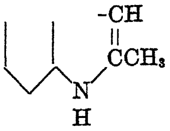
isoquinoline (89)

(1353) $C_9H_7NO_2$



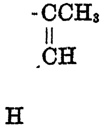
indole-2-carboxylic acid (90)

(1354) C_9H_9N



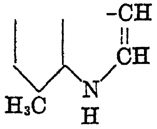
2-methylindole (90)

(1355) C_9H_9N



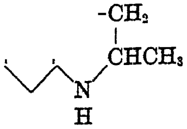
3-methylindole (90)

(1356) C_9H_9N



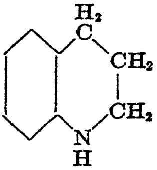
7-methylindole (90)

(1357) $C_9H_{11}N$



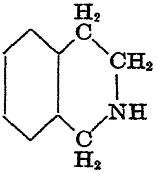
2,3-dihydro-2-methylindole (90)

(1358) $C_9H_{11}N$



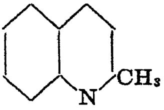
tetrahydroquinoline (89)

(1359) $C_9H_{11}N$



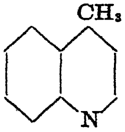
tetrahydroisoquinoline (89)

(1360) $C_{10}H_9N$



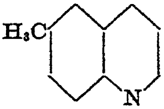
quinaldine (89)

(1361) $C_{10}H_9N$



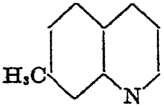
4-methylquinoline (89)

(1362) $C_{10}H_9N$



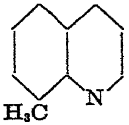
6-methylquinoline (89)

(1363) $C_{10}H_9N$



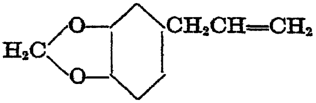
7-methylquinoline (89)

(1364) $C_{10}H_9N$



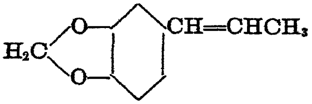
8-methylquinoline (89)

(1365) $C_{10}H_{10}O_2$



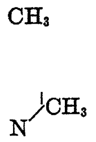
safrole (456)

(1366) $C_{10}H_{10}O_2$



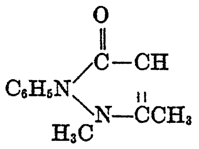
isosafrole (299, 301)

(1367) $C_{11}H_{11}N$



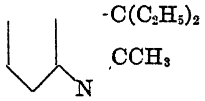
2,4-dimethylquinoline (89)

(1368) $C_{11}H_{12}N_2O$



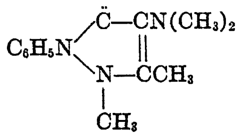
antipyrene (89)

(1369) $C_{13}H_{17}N$



3,3-diethyl-2-methylindolenine (90)

(1370) $C_{13}H_{17}N_3O$



pyramidone (89)

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[2] In naming these compounds the Geneva system was used generally for the higher members of the series. Whenever in the literature two names were used—the Geneva system name and one more commonly employed—the compound was indexed under the latter. The iso compounds were indexed under "iso". The prefixes "secondary" and "tertiary" were disregarded in placing names containing them in the index. When two or more radicals appeared in a name, they were listed in the order of increasing size.

[3] The numbers following the names of the compounds refer to the "formula numbers" used in the formula index.

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ERRATA[5]

Page 355. In equation 5 the first ν should be $\bar{\nu}$.
The next to the last line should read "the mean restoring force is $1/2\bar{a}F$ and the necessary energy is $1/2\bar{a}^2F$, which may be equated to $h\nu c$,"
In the last equation substitute $2\pi^2$ for $4\pi^2$.
Page 393. The figure attributed to Segré should be attributed to Bolla.
Page 453. In line 19, R—C═N should read "R—C≡N."
Page 470. Reference 172 should read "Mecke"; reference 173 should read "Mecke and Baumann"; reference 174 should read "Mecke and Freudenberg."
Page 477. In section V, read "Carelli and Went" for "Carelli and West."

All references to the work of Kohlrausch and associates published in the *Sitzungsberichte,* as well as references 42, 56, and 57, should read "Abt. a" instead of "Abt. b."

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[5] These corrections are to be made in the previous article by Hibben (Chem. Rev. **13**, 345 (1933)).

A SYMPOSIUM ON THERMODYNAMICS[1]

MODERN THERMOCHEMISTRY[2]

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I. INTRODUCTION

It is the purpose of this paper to present a picture of thermochemistry in relation to modern chemical thermodynamics, to discuss briefly the principles and methods of accurate thermochemical measurements, and to make certain suggestions and proposals for making the data of thermochemistry more uniform and reliable, and increasing their utility in chemical thermodynamics.

The aim of thermochemistry, which may be formally defined as that branch of chemical thermodynamics which treats of the changes in internal energy or heat content associated with chemical reactions, is to provide the experimental data for compiling a table of values from which may be calculated the heat of every possible chemical reaction. This table may be called the thermochemical table. The necessity of having accurate values of ΔH, the increment in heat content, for every process or reaction[3] is readily apparent to those engaged in almost any variety of calculation in chemical thermodynamics.

The ultimate end of chemical thermodynamics may be said to be the evaluation of the free energy of formation, from the appropriate fundamental units of matter, of every substance in all possible states, but the attainment of this end will be made possible only by the utilization of many indirect methods of calculation, and the proper combination of what may at first sight appear to be only remotely related experimental data. From the standpoint of the compilation of the ultimate or master table of chemical thermodynamics, the most important thermodynamic properties, in addition to the free energy itself, are the heat content and the entropy; and the successful evolution of the master table is predicated upon the existence of accurate values of the heats of formation and of the entropies of formation.

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[1] This Symposium was held by the Division of Physical and Inorganic Chemistry at the Ninetieth Meeting of the American Chemical Society, in San Francisco, August 21, 1935, under the chairmanship of J. H. Hildebrand and with an introduction by Gilbert N. Lewis. The final paper in the Symposium, by Dr. Merle Randall of the University of California, entitled "Stoichiometry and the Correlation of Thermodynamic Data," was not submitted in time for inclusion in this publication.

[2] Publication approved by the Director of the National Bureau of Standards, United States Department of Commerce.

[3] The symbols and nomenclature used in this paper are those of Lewis and Randall (22). For any reaction, ΔH (or ΔF or ΔS) is equal to the sum of the heat contents (or free energies or entropies) of the products less the sum of the heat contents (or free energies or entropies) of the reactants, each substance being in a defined physical state at the given temperature.

In the master table there will appear for each substance values of ΔH, ΔS, and ΔF, the heat, entropy, and free energy of formation, respectively. For each temperature, all the values in the table should possess both "vertical" and "horizontal" consistency. "Vertical" consistency is assured when, at a given temperature, each value of ΔH (or of ΔS, or of ΔF) is in accord with all the other values of ΔH (or of ΔS, or of ΔF) with which it can be correlated by means of experimental data. With all the values in the table being "vertically" consistent, then the calculation of the values of ΔH (or of ΔS, or of ΔF) for any given reaction will be independent of the path (or the particular values which happen to be added or subtracted). "Horizontal" consistency in the table is assured when, for each temperature, the values recorded for ΔH, ΔS, and ΔF for each substance are in accord with the relation,

$$\Delta F = \Delta H - T\Delta S$$

This "horizontal" consistency will be automatic for all those substances for which independent values of only two of the three properties are available, but for the remainder this cross-checking will serve to increase the accuracy and reliability of the entire table. In order to facilitate the correlation, each value in the table should be written so as to indicate both its absolute and its relative accuracy.

The manner of assembling such a master table of chemical thermodynamics may be somewhat as follows: There will first be built up separate independent tables of values of ΔH, ΔS, and ΔF, for some selected standard temperature, say 25°C. The ΔH table will contain only values derived from calorimetric data on heats of reaction; the ΔF table will contain only values derived from data on equilibria; and the ΔS table will contain values derived from spectroscopic data, or from experimental data on heat capacities down to near the absolute zero, or from experimental data on the temperature coefficient of ΔF. The separate tables are, at this juncture, completely independent, and, after each table is made properly self-consistent "vertically," may be brought together to form the nucleus of the master table. It is at this point that the cross-checking for "horizontal" consistency will be made for all those substances for which there are independent values of all three properties. It is obviously necessary that the values of ΔH, $T\Delta S$, and ΔF be recorded in the same unit of energy if this cross-checking is to be significant, and therefore, all the original data must be accurately expressible in terms of fundamental units. When, by proper adjustment, the three columns have been brought into "horizontal" consistency, the value of the third property may be computed for those many substances for which there will be known the values of only two of the properties. There will be in the table a large number of substances for which the value of but one of the three properties is known; and, in addition, there will be a very large number of known substances not appearing in the table because no data at all are available. It will be the next order of business for the experimenters in chemical thermodynamics to supply these needed data.

The foregoing picture indicates the relation of thermochemistry to the general scheme of the data of modern chemical thermodynamics. Before the master table can be assembled, adequate and accurate tables of ΔH, ΔS, and ΔF must be prepared, and it is the work of thermochemistry to supply the fundamental data for the first of these.

II. THE RENAISSANCE IN THERMOCHEMISTRY

About fifteen years ago, thermochemistry began to undergo a sort of renaissance (33). In order to understand this phenomenon one must look back to the middle of the nineteenth century. At that time, Julius Thomsen at Copenhagen and Marcellin Berthelot at Paris were beginning their work in thermochemistry, and each independently announced the theorem that the heat of formation of a substance is a direct measure of the chemical affinity. Spurred on by this belief, Thomsen and Berthelot amassed an enormous amount of thermochemical data, their work reaching its zenith at about the time of the publication of Thomsen's monumental four volumes on thermochemistry, in 1882–86.

It was some years before this, however, that the second law of thermodynamics began to make its way into chemistry, and its true relation to chemical reactions was being developed by Clausius, Gibbs, Helmholtz, van't Hoff, and others. It was then shown that the true measure of the chemical affinity is not the heat content, H, but the heat content less the product of the entropy and the absolute temperature, $H - TS$, which function is now termed the free energy.

Before the close of the nineteenth century, both Thomsen and Berthelot reluctantly accepted the second law, which had caused the relegation of their great body of thermochemical data to a relatively minor place in the science, and experimenters turned their attention to those measurements which would yield true values of chemical affinity. The decline in thermochemical research continued with but minor halts until some ten or fifteen years ago, when two new developments brought about a radical change in the status of thermochemical data in relation to chemical thermodynamics. The developments which lifted the data of thermochemistry to a new position of importance in the science were: first, the determination of the entropies of substances by measurement of their heat capacities and latent heats down to low temperatures and utilization of the resulting data according to the third law; and, second, the calculation of certain thermodynamic quantities from a combination of statistical mechanics with the data of spectroscopy. With certain important limitations on the first, each of these methods yields values of the entropy independent of other experimental data; so that it is possible to compute values of ΔF by combining values of ΔS, obtained in the above manner, with values of ΔH, obtained from calorimetric data. There are a very great number of substances, especially among the organic compounds, for which values of the free energy can not be determined from equilibrium experiments. The methods of determining entropies by means of spectroscopic data and the third law are, therefore, extremely important; furthermore, they place a premium upon accurate thermochemical data, because, in most cases, the relative magnitudes and absolute accuracies of the values of ΔS and ΔH are such that the resulting uncertainty in ΔF is practically equal to the error in ΔH.

Now at this time the great body of thermochemical data was still founded upon the prodigious work of Thomsen, Berthelot, and their coworkers of the period before 1900, but their data, while more than accurate enough for the nineteenth century, fell far short of meeting the new requirements. This inadequacy of their data was no reflection upon the work of these pioneers in thermochemistry, who performed extraordinarily well with their meager apparatus in spite of considerable handicaps (such as the frequent lack of pure materials), but rather was evidence of the great advances which had taken place in chemical thermodynamics.

It is at this point that the renaissance in thermochemistry may be said to have begun. It became evident that the time was overdue for a redetermination of the important thermochemical values, in terms of a fundamental unit of energy, and with an accuracy as high as would be possible with the improved calorimetric apparatus and technique and the pure materials available today.

III. THE THERMOCHEMICAL TABLE

The ideal thermochemical table is one which will permit calculation of the heat of every chemical reaction. Obviously it would be impractical to list in a table the heat of every reaction, but the same end is accomplished by listing for each chemical substance its heat of formation from the elements in selected standard states. This is the scheme that has been used since the middle of the last century. It is evident that, by proper selection, the number of chemical reactions whose heats must be measured will be about the same as the number of substances listed in the table. Some saving in the number of reactions to be measured will occur among the organic compounds because of certain simplifying rules for the energy increment per CH_2 group in aliphatic radicals (34).

The value of the heat of formation of a given substance may be the result of the determination of the heat of one reaction, as for H_2O (liq.):[4]

$$H_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) = H_2O(\text{liq.})$$

For many other substances, however, the value will result from the measurement of the heats of a number of chemical reactions, as for NaOH(c):

$$\begin{array}{rcl} Na(c) + H_2O(\text{liq.}) &=& NaOH(\text{aq.}) + \tfrac{1}{2}H_2(\text{gas}) \\ H_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) &=& H_2O(\text{liq.}) \\ NaOH(c) &=& NaOH(\text{aq.}) \\ \hline Na(c) + \tfrac{1}{2}O_2(\text{gas}) + \tfrac{1}{2}H_2(\text{gas}) &=& NaOH(c) \end{array}$$

There will be certain basic values in the table which will be used very frequently in the derivation of other values. These basic values, which should be known with considerable accuracy, include the heats of formation of water, carbon dioxide, nitric acid, sulfuric acid, hydrogen chloride, hydrogen sulfide, and others. Because of this interdependence of many of the values of heats of formation, it is extremely desirable that values for the important thermochemical constants be carefully selected, and, when any change is made in any one of the basic values, corresponding changes should be made in all the values which depend upon it. It is for this same reason that the addition or subtraction of values of heats of formation from different tables is a very precarious undertaking. What is needed is one table of values that will be used universally.

In setting up the primary table of heats of formation, it is necessary to select a standard temperature for the entire table and a standard state for each substance. The most useful and convenient standard temperature is one at or near room temperature, and, following the convention already adopted for the standard free energy values by Lewis and Randall, one can select 25°C. as a desirable standard temperature. The standard state of each element, in which it will be assigned a reference heat content of zero for the purposes of this table, can be that state in which the element naturally exists at the standard temperature and at a pressure of 1 atmosphere. For gases, the standard state would more exactly be that hypothetical standard state of unit fugacity (22), where the heat content is the same as that of the real gas at zero pressure at the given temperature. It is important to note that this hypothetical standard state of unit fugacity (1 atmosphere) is not that real state of the gas in which it has a fugacity equal to 1 atmosphere. For a large number of gases, at 25°C., the heat content at 1 atmosphere is not significantly (at present) different from its heat content at zero pressure.

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[4] The abbreviations used to indicate phases are as follows: c = crystal; liq. = liquid; aq. = aqueous.

IV. UNITS OF ENERGY

As pointed out in an earlier part of this paper, all thermodynamic values of ΔF, $T\Delta S$, and ΔH must be expressed in terms of a common unit of energy, otherwise the intercombination of values from the various sources will be inaccurate and may lead to disconcerting results. For a number of reasons, the logical and desirable unit of energy is the erg, the fundamental C.G.S. unit; particularly to be avoided are units of energy defined in terms of the properties of any substance, such as water. In order for it to have a real utility in chemical thermodynamics, a thermochemical value must therefore be expressible, so far as is significant, in terms of the fundamental unit of energy. This is easily accomplished today by using electrical energy, as from a lead or other storage battery, for comparison with the energy of the chemical reaction.

Electrical measurements of energy are based upon the second as the unit of time and upon working standards of electromotive force and resistance maintained at the various national standardizing laboratories. The working standards now universally used in these laboratories are wire (usually manganin) resistance coils and saturated cadmium (Weston) cells, which are calibrated in terms of the international ohm and the international volt. When originally established in 1908, the international units, defined in terms of the mercury ohm and the silver voltameter, were identical with the absolute units within the limits with which the latter could then be determined (15). Since that time, however, the accuracy of the absolute measurements has increased, and more accurate determinations of the absolute ohm and the absolute ampere have been made (10, 13, 40, 41). The results indicate that the international joule[5] is greater than the absolute joule (= 10^7 ergs) by about 0.04 per cent (6, 7, 10, 43).

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[5] It should also be pointed out that although the working standards (wire resistances and saturated cadmium cells) of the various national standardizing laboratories of England, France, Germany, and the United States were given the same values in 1910, the standards in the different countries have diverged a little since then. The international joule as derived from standards maintained at the National Bureau of Standards has differed from that of the other countries by amounts ranging from 0.006 to 0.014 per cent (44).

All measurements of electrical energy made since about 1910 by means of standard cells and standard resistances are actually in terms of the international joule. This is also true of all similar measurements that will be made until such time in the future as the various national standardizing laboratories begin to calibrate standard cells and resistances in terms of absolute units. It is the expectation of the Advisory Committee on Electricity of the International Committee on Weights and Measures that the old "international" standards set up in 1908, the mercury ohm and silver voltameter, will be discarded; that the working standards, saturated cadmium (Weston) cells and wire resistances, will be periodically calibrated in terms of the absolute units; and that all the national standardizing laboratories will adjust their units as soon as common international action can be obtained, to absolute values that will be decided upon by the International Committee from the results of the new determinations of the absolute ohm and absolute ampere that are now near completion in the various national laboratories (10, 43).

Values of ΔH, ΔF, and $T\Delta S$ will have their greatest utility in chemical thermodynamics if they are all expressible in the fundamental unit of energy, the erg (or the absolute joule $= 10^7$ ergs), or in terms of an arbitrary unit derived from the fundamental unit by pure definition.

The most accurate direct values of ΔH are today determined calorimetrically in terms of the international joule, which can be converted to the absolute joule by means of an appropriate factor.

Direct experimental values of ΔF can be determined from equilibrium measurements or from the electromotive force of cells. In the first case, ΔF is derived from the relation involving $RT\ln K$, and the value of ΔF depends upon the units of RT, the product of the gas constant and the absolute temperature. The product RT is equal to the product PV for an ideal gas at the given temperature, and, when P is expressed[6] in dynes per square centimeter and V in cubic centimeters, the unit of energy is the erg. In the second case, ΔF is derived from the relation involving $N\mathcal{F}\mathfrak{E}$, and the value of ΔF depends upon the unit of the electromotive force $\mathfrak{E}$ and the Faraday constant $\mathcal{F}$. At the present time, $\mathfrak{E}$ is measured in international volts. The value of $\mathcal{F}$ is determined experimentally from the atomic weight of silver and the electrochemical equivalent of silver, the latter being defined as that mass of silver carried by 1 international ampere of current in 1 second. The quotient of the atomic weight and the electrochemical equivalent gives the value of $\mathcal{F}$ in international joules/(international volt × equivalent). And the product of $N\mathcal{F}\mathfrak{E}$ gives international joules, which can be converted to absolute joules by means of the appropriate factor.

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[6] It is true that P is not usually measured in dynes per square centimeter, but the unit ordinarily used can be converted to dynes per square centimeter with an accuracy of better than 0.001 per cent.

Independent values of $T\Delta S$ can be obtained in two ways. In the first place, the utilization of measurements of the heat capacity down to low temperatures according to the third law yields values of $T\Delta S$ in terms of international joules, which can be converted to absolute joules by means of the appropriate factor. In the second place, values of $T\Delta S$ can be calculated from spectroscopic data (and the Sackur-Tetrode-Stern equations) by statistical methods, and the value of $T\Delta S$ depends upon the units of RT. As before, this product is evaluated from a knowledge of the product PV for an ideal gas at the given temperature, and the energy is in ergs when P and V are in dynes per square centimeter and in cubic centimeters, respectively.

The foregoing discussion shows that values of ΔH, ΔF, and $T\Delta S$ are determined, independently of one another, in terms of the international or the absolute joule, and that, therefore, the values can all be expressed in terms of the absolute joule and combined with one another without fear of error due to inconsistent units. Since many thermodynamic calculations involve the combination of large numerical quantities to obtain a relatively small quantity, as for example,[7]

$$(\Delta F)_1 - [(\Delta H)_2 - T(\Delta S)_2] = (\Delta F)_3$$

it is imperative that all the quantities be expressed in units of the same size as well as the same name.

It would seem, therefore, that every branch of modern chemical thermodynamics is forced to accept the erg or absolute joule as the real unit of energy, and that all accurate thermodynamic values of energy, whether ΔH, ΔF, or $T\Delta S$, no matter how derived or in what units expressed, really arise from the absolute unit. This being the case, it is extremely desirable that chemical thermodynamics divorce itself completely from any unit of energy which is expressed as a property of some substance, such as that calorie which is defined in terms of the heat capacity of water.

About ten years ago, the late E. W. Washburn hoped that chemists might be prevailed upon to express their values of energy in terms of the absolute joule, and to that end F. R. Bichowsky used the absolute joule as the unit of energy in the thermochemical section of the International Critical Tables (16). But this change from calories to joules was apparently not received with favor by the great majority of chemists, and it appeared that the calorie would at least have to be retained as the name of the unit of energy. It was also realized that there would have to be separated from the new calorie every connection with the heat capacity of water, else one would have to change all the thermodynamic values every time someone determined the heat capacity of water with an accuracy greater than that already existing.

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[7] The subscripts here indicate different reactions.

While there was justification in the time of Thomsen and Berthelot for using a unit of energy defined in terms of the heat capacity of water, the necessity for that awkward and not very accurate procedure disappeared about twenty-five years ago, when it became possible to measure quantities of energy much more accurately in terms of the absolute unit of energy by means of a potentiometer, standard cell, and standard resistances.

The situation with regard to the unit of energy in modern chemical thermodynamics may be summarized as follows: First, the actual unit of energy is the absolute joule, and all thermodynamic values should primarily be expressed in terms of that fundamental unit. Second, for historical, psychological, or other reasons, the values of chemical thermodynamics may be given also in terms of a unit of different size than the absolute joule having the name "calorie," which is derived from the absolute joule by means of an arbitrary factor set up by definition and universal agreement. The resulting calorie is a defined conventional unit bearing a constant unchanging relation to the absolute joule; and, furthermore, this calorie has no connection whatever with the heat capacity of water, although its numerical value is incidentally approximately equal to, and its name is historically derived from, the amount of heat energy required to raise the temperature of one gram of water through one degree Centigrade.

In 1930, the thermochemical laboratory of the National Bureau of Standards began to report thermochemical values having an estimated uncertainty as low as 0.02 per cent, and it was, therefore, necessary that a uniform policy for recording these values be established. Following the recommendation made at that time by the Division of Electricity at the National Bureau of Standards (43), the following was accepted as the true relation between the international joule and the absolute joule, with an error of less than 1 part in 10,000:

$$\text{1 international joule} = \text{1.0004 absolute joules}^{8}$$

Then the following arbitrary definition of the calorie was made:

$$\text{4.1850 absolute joules} \equiv 1\ \textit{calorie}$$

So that

$$\text{4.1833 international joules} = \text{4.1850 absolute joules} \equiv 1\ \textit{calorie}$$

Since 1930, all the thermochemical values from this laboratory have been reported in the unit in which they were measured, the international joule,

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[8] See also references 6 and 7.

and converted to a conventional *calorie*, defined by means of the above relations. Fortunately, the other laboratories in the United States which are making energy measurements in chemical thermodynamics have accepted, by more or less tacit consent, the same relations, so that in this country at least there seems to be a uniformity of procedure in this regard.

It is suggested that, in order to avoid the confusion resulting from different sizes of units of energy with the same name, as has frequently occurred in the past history of thermodynamics and thermochemistry, all values of energy in chemical thermodynamics be reported in accord with the foregoing relations. When the national standardizing laboratories begin calibrating standard cells and resistances in absolute instead of "international" units, and when a more accurate relation between the international joule and the absolute joule is agreed upon by the national standardizing laboratories, the foregoing relations can be appropriately altered.

In the evaluation of free energies and entropies, the values assigned to the gas constant, R, the Faraday constant, $\mathcal{F}$, and the absolute temperature of the ice point, $T_{0^\circ\text{C.}}$, should be consistent[9] with the best existing experimental values of $(PV)^0_{0^\circ\text{C.}}$, $T_{0^\circ\text{C.}}$, the atomic weight of silver, and the electrochemical equivalent of silver. As already pointed out, the energy units of R and $\mathcal{F}$ come out directly as absolute joules and international joules, respectively, and the conversion to the defined conventional *calorie* may be made by the relations given above.

It would be very desirable if a Committee on Chemical Thermodynamics were established to survey the existing data and establish values of R, $T_{0^\circ\text{C.}}$, $\mathcal{F}$, and other pertinent constants that would be universally accepted. This would make for a uniformity in the data of chemical thermodynamics, which is now lacking.

V. REQUISITES OF THE CHEMICAL REACTIONS TO BE MEASURED

In order to determine the value of the heat of formation of a substance, one selects for measurement reactions in which all the reactants and products, save the given substance, have known heats of formation. In a few cases it is possible to utilize the direct reaction of synthesis of the given substance from its elements in their standard states.

The chemical reactions whose heats are to be measured must fulfill

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[9] For example, the values assigned to R and $T_{0^\circ\text{C.}}$ must be such as to satisfy the relation:

$$RT_{0^\circ\text{C.}} = (PV)^0_{0^\circ\text{C.}} = (1{,}013{,}250)\,(22{,}414.1) = 2{,}271.11 \times 10^7 \text{ ergs} = 2{,}271.11 \pm 0.08 \text{ absolute joules.}$$

That is to say, while the uncertainty in the value of $T_{0^\circ\text{C}}$. may be about 1 part in 14,000, the uncertainty (6) in the value of $RT_{0^\circ\text{C.}}$ is only 1 part in 28,000.

certain requirements under the conditions of the calorimetric experiment. First, each reaction must be one which proceeds to completion, and which is not significantly contaminated with side reactions, except so far as these can be accurately corrected for; and, second, each reaction must be one whose amount can be accurately measured.

VI. PRINCIPLE OF THE MODERN THERMOCHEMICAL METHOD

The principle of the modern experimental method in thermochemistry is to carry out the reaction to be studied in the calorimeter in such a manner that it will be possible to compare the heat evolved by the chemical reaction with the heat evolved by electrical energy, or by a measured amount of a standard chemical reaction, the heat of which has already been compared with electrical energy.

If the given reaction is one which evolves heat energy, then the comparison of the chemical energy with electrical energy can be made by performing two kinds of experiments: chemical reaction experiments and electrical energy experiments. In each of these experiments the calorimeter system is the same throughout. In the first kind of experiment, a measured amount of chemical reaction is used to bring the calorimeter system from an initial temperature T_A to a final temperature T_B. In an experiment of the second kind, a measured amount of electrical energy is used to bring the identical calorimeter system from the same initial temperature T_A to the same final temperature T_B. In this manner one obtains a comparison between a measured amount of chemical reaction and a measured amount of electrical energy, using the calorimeter as the absorber and comparator of the two kinds of energy.

This substitution method eliminates many of the usual calorimetric errors because of their cancellation in the two kinds of experiment, which are practically identical except that in one case the energy is electrical and in the other chemical. Furthermore, this method makes it unnecessary to know anything about the heat capacity of the calorimeter system or any of its parts, or to know the exact size of a degree of temperature, as is required in determinations of heat capacity. It is necessary only that the thermometric device used be sensitive enough to reproduce accurately and with sufficient precision the initial and final temperatures.[10] A knowledge of the actual temperature on the Centigrade scale is needed only to determine the temperature at which the reaction may be said to have taken place, and the absolute accuracy with which this reaction temperature

[10] Actually, of course, it is necessary only that the initial and final temperatures in the different experiments be identical within a certain known small amount, because the subsequent small correction of the various initial (or final) temperatures to a common initial (or final) temperature can be made without loss of accuracy.

must be known depends upon the accuracy of the resulting thermochemical value and upon the magnitude of the temperature coefficient of the heat of the given reaction. Even for work of the highest accuracy and for reactions having a relatively large value of ΔC_p, the reaction temperature need be known only to about 0.01°C.

For reactions in which heat energy is absorbed, the comparison of the chemical energy with electrical energy may be made in the same experiment by adding to the calorimeter electrical energy at the same rate and of the same amount as is being absorbed by the reaction, so that the temperature of the calorimeter remains sensibly unchanged throughout the experiment. In this case, however, appropriate subsidiary observations must be made to determine the actual amount of the stirring energy, evaporation energy, etc.

Whenever it is not possible to determine an amount of electrical energy with the necessary accuracy and precision, one may utilize as the source of the "calibration" energy a "standard" chemical reaction, of the same type as the unknown, which has previously been accurately compared with electrical energy in a standardizing laboratory.

VII. TYPES OF REACTIONS

Nearly all the chemical reactions whose heats require measurement can be grouped into three classes according to the type of reaction and the corresponding calorimetric method which must be employed:[11]

1. Reactions substantially in the gaseous phase at constant pressure.
2. Reactions substantially in the liquid phase at constant pressure.
3. Reactions in a closed bomb at constant volume.

The reactions of the first class are carried out at constant pressure in a reaction vessel in the calorimeter, the reaction taking place in a flame or at the surface of a catalyst. Examples of this class include the following:

$$H_2(\text{gas}) + \tfrac{1}{2}O_2(\text{gas}) = H_2O(\text{liq.})$$
$$\tfrac{1}{2}Cl_2(\text{gas}) + \tfrac{1}{2}H_2(\text{gas}) = HCl(\text{gas})$$
$$CH_4(\text{gas}) + 2O_2(\text{gas}) = CO_2(\text{gas}) + 2H_2O(\text{liq.})$$
$$C_2H_4(\text{gas}) + H_2(\text{gas}) = C_2H_6(\text{gas})$$
$$O_2(\text{gas}) + S(\text{c}) = SO_2(\text{gas})$$

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[11] The present discussion does not include that class of reactions involving atomic energies, such as the dissociation of gaseous molecules into atoms, energies of excitation (rotational, vibrational, and electronic), and energies of ionization, which cannot be measured calorimetrically, except in isolated instances (5, 9, 29), but are determined by analyzing the appropriate experimental data of spectroscopy and electron bombardment measurements according to acceptable theories of atomic and molecular structure.

As actually carried out in the calorimeter, the second substance given in each of the first four of the foregoing examples is, for the practical purpose of obtaining completeness of reaction or accuracy in the determination of the amount of reaction, in excess of the stoichiometrical amount, except that in the first reaction hydrogen may be in excess without disadvantage. The last reaction is one in which, while the sulfur is in the solid state at the beginning and at the end of an experiment, the reaction actually occurs in a flame with oxygen burning in an excess of sulfur in the gaseous phase, in order to prevent the formation of sulfur trioxide (12).

The rate of evolution of heat energy in the above reactions as they proceed in the calorimeter is controlled by the rate at which the gas which is not in excess is fed into the reaction vessel, and can, therefore, be maintained practically constant at an appropriate value for the duration of an experiment.

The determination of the amount of reaction in the above reactions can usually be most accurately and conveniently made by determining the mass of one of the substances formed, rather than the mass of one of the substances used up.

The reactions of the second class are carried out at constant pressure in a reaction vessel which is usually itself the calorimeter, the reaction resulting from the mixing of two liquids, or of a solid and a liquid, or of a gas and a liquid. Examples of this class include the following:

$$\mathrm{HCl\cdot100H_2O(liq.) + NaOH\cdot100H_2O(liq.) = NaCl\cdot201H_2O(liq.)}$$
$$\mathrm{HCl(gas) + 100H_2O(liq.) = HCl\cdot100H_2O(liq.)}$$
$$\mathrm{NaCl(c) + 100H_2O(liq.) = NaCl\cdot100H_2O(liq.)}$$
$$\mathrm{NaCl\cdot100H_2O(liq.) + 100H_2O(liq.) = NaCl\cdot200H_2O(liq.)}$$
$$\mathrm{NaCl(aq.) + AgNO_3(aq.) = AgCl(c) + NaNO_3(aq.)}$$
$$\mathrm{Na(c) + H_2O(liq.) = NaOH(aq.) + \tfrac{1}{2}H_2(gas)}$$

In some of the above reactions, the rate of evolution of heat energy can be controlled by the appropriate mixing of the two reacting substances, while in others the mixing is carried out at one stroke, in which case the heat energy is evolved or absorbed exponentially with time.

In reactions of this type, the amount of reaction is usually determined from the amounts of each of the initial substances. Because concentration is an important variable, this must be accurately known for all the reactants and the product. Furthermore, the extent of completion of the reaction must be ascertained from a knowledge of the free energies in the system formed in the reaction.

The reactions of the third class are carried out in a closed bomb at constant volume and, with a few exceptions, are all combustion reactions, in which a gas, liquid, or solid is burned with an excess of oxygen. Most of the substances so burned are organic compounds, and the main products of combustion are carbon dioxide and water. Because the reaction is in the nature of an explosion, the entire amount of heat is evolved in a very short period of time. While this type of reaction can be carried out quickly and simply with a bomb calorimeter, the calorimetric data can not always be interpreted with the highest accuracy because of the complex nature of the system existing in the bomb at the end of the experiment (see page 251).

VIII. THERMOCHEMICAL CALORIMETRY AND THERMOMETRY

Fortunately for present-day investigators in thermochemistry, the apparatus and technic of calorimetry have been developed to such a high degree of precision and accuracy that measurements of quantities of energy can be made with uncertainties as low as 0.01 or 0.02 per cent. The main calorimetric problem of the thermochemist, then, is to adapt the existing apparatus and technic to the determination of the heat of a particular chemical reaction.

The apparatus, technic, and procedure of modern calorimetry have been described at considerable length by a number of writers (11, 18, 28, 30, 46), to whose publications the reader is referred for detailed information on the subject of modern calorimeters and calorimetric thermometry. It is important to remember at this point that the investigator who is determining the isothermal heat of a chemical reaction has an advantage, in point of accuracy, over the one who is determining the heat capacity of a substance, or its increase in heat content between two temperatures. The former need only duplicate the apparent temperature rise of the calorimeter under the given conditions, while the latter must determine the true temperature rise of the calorimeter in absolute degrees.[12]

The type of calorimetric method to be used in a given thermochemical investigation is determined by the type of reaction to be studied. Nearly all the reactions susceptible of thermochemical measurement can be grouped into the three classes listed on page 244, and the different types of calorimetric apparatus and procedure may accordingly be said to fall into three classes.

Examples of modern calorimetric apparatus and procedure used in studying reactions of the first class, those occurring substantially in the gaseous phase at constant pressure, are those employed at the National Bureau of Standards and at several other laboratories (12, 20, 30). A detailed description of these assemblies and procedures is given in the papers cited.

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[12] An exception is the determination, by the dropping method, of the decrease in heat content of a substance between a high temperature and that of the calorimeter (near room temperature), in which case the investigator can, as in the measurement of the heat of a reaction, duplicate the temperature rise of the calorimeter, whatever it may be, by means of electrical energy. While in this case the temperature rise of the calorimeter need not be known accurately, in absolute degrees, the difference between the initial and final temperatures of the substance under investigation must be so known.

For measuring the heats of reactions of the second class, those occurring substantially in the liquid phase at constant pressure, precise calorimetric apparatus and procedure have been developed in a number of laboratories (8, 21, 23, 25, 26, 28, 37, 39). Although extremely precise, some of these calorimetric assemblies have lacked an important feature of accurate modern thermochemical work, that of providing a means for reproducing, by means of electrical energy, the change in the calorimeter brought about by the energy of the chemical reaction.

The calorimetric apparatus for measuring the heats of chemical reactions of the third class, those occurring at constant volume in a closed bomb, is well standardized, and a detailed description of the modern apparatus and technic is given in a number of papers (11, 17, 18, 19, 27, 37, 38, 42). While the bomb calorimeter is susceptible of very high precision, approaching 0.01 per cent in some cases, two points in connection with the accuracy of the thermochemical values obtained should be noted. In the first place, if the assembly lacks an electrical energy circuit, the electrical energy equivalent of the calorimeter must be determined, as indicated on page 248, by means of a "standard" reaction carried out under certain given conditions. In the second place, the reaction which actually occurs in the bomb is never a completely clear cut one, and some very significant corrections to standard states must be made (see page 250).

IX. DETERMINATION OF THE ELECTRICAL ENERGY EQUIVALENT OF THE CALORIMETER

The electrical energy equivalent of the calorimeter is the amount of electrical energy required to bring the calorimeter from the initial temperature T_A to the final temperature T_B under the same calorimetric conditions as exist for the chemical reaction experiments, T_A and T_B being, respectively, the same in all the experiments.

Though the electrical energy equivalent of the calorimeter, per degree rise in temperature, approximates the heat capacity of the calorimeter, the latter term should be entirely avoided in experimental thermochemistry. There are several reasons for this. In the first place, the actual determination of the heat capacity of the calorimeter would require not only the accurate and precise calibration of the thermometer in terms of the true temperature scale, but also the definition of the physical limits of the system whose temperature is to be raised by the measured energy. Both of these requirements involve a considerable expenditure of effort and they are wholly superfluous, since the thermochemical values will in no way be made more accurate because of them. In the second place, the term "heat capacity of the calorimeter" carries, from the early days of thermochemistry, the implication that the value may be derived by summing the heat capacities of the parts of the system. Such a procedure is far too inaccurate for the requirements of modern thermochemistry, where it is desired to know accurately the energy required to take the calorimeter system from a given initial state to a given final state under the same calorimetric conditions as obtain in the reaction experiments.

The effect of possible calibration errors in the resistance thermometer and bridge, or in the thermoelement and potentiometer, can be entirely eliminated by using the same thermometric system in all the experiments and making both electrical energy and chemical reaction experiments over the same temperature interval.

Insofar as is possible, the rate of temperature rise should be made practically the same in both the experiments with electrical energy and those with chemical energy. This requirement is easily met in the experiments on reactions of the first class (see page 244), but with more difficulty for reactions of the second and third classes. The reactions occurring in the bomb calorimeter are probably the most difficult in which to match the rate of input of electrical energy with the rate of evolution of chemical energy. The more alike are the time–temperature curves in the two kinds of experiments, the less danger is there that errors in the corrections for heat flow into the calorimeter from the jacket and surroundings will fail to cancel.

The measurement of electrical power is most conveniently and accurately made by measuring the potential drop across the heating coil in the calorimeter and the current passing through it (the latter being determined by measuring the potential drop across a standard resistance in series with the heating coil). The accuracy of the measured value of the electrical energy then depends upon the accuracy of the device used for measuring the time of input of the electrical energy, and the accuracy of calibration of the electromotive force of the standard cell and the resistance of the coils of the potentiometer and the standard resistance.

When the necessary electrical and timing apparatus is not available for making a direct determination of the electrical energy equivalent of the calorimeter, a "standard" chemical reaction is used as the source of the calibrating energy. In the bomb calorimeter, for example, a standard sample of benzoic acid can be used, though it is important for accurate work that the benzoic acid be burned under the same conditions as in the standardizing laboratory. In a constant-pressure flame calorimeter the reaction between hydrogen and oxygen to form water may similarly be used to provide the "standard" energy (24, 30, 45).

X. EXAMINATION OF THE PURITY OF THE REACTION

One phase of thermochemical research that has often received too little attention in the past is the problem of examining the purity of the chemical reaction being studied. The investigator should demonstrate with reasonable certainty, by means of appropriate chemical or physical tests, that the reaction which actually occurs in the calorimetric reaction vessel is one which does not differ significantly, with regard to the evaluation of the given thermochemical constant, from the theoretically pure reaction. Or, if there is a side reaction, the amount and effect of it must be evaluated with the necessary accuracy.

Having first decided that the reaction being studied is reasonably complete and clear cut, one can investigate the purity of the reaction as it actually occurs, first by establishing the purity of the reacting substances, and second by examining the products of the reaction for the presence of possible foreign substances. The permissible amounts of impurities in the reacting substances, and the permissible amounts of side reactions, depend to a large extent upon the method by which the amount of the reaction is determined and upon the amount of heat energy contributed by the side reactions involved.

XI. DETERMINATION OF THE AMOUNT OF REACTION

One of the vital points in any thermochemical investigation is the method of determining the amount of chemical reaction which occurs in any given experiment. The method selected should be precise and accurate with respect to true mass in grams, and the amount should be accurately expressible in terms of moles. This latter requirement involves an accurate knowledge of the molecular weight of the substance whose mass determines the amount of reaction.

Suppose, for example, that the reaction being studied is

$$C_6H_{14}(\text{liq.}) + \tfrac{19}{2}O_2(\text{gas}) = 6CO_2(\text{gas}) + 7H_2O(\text{liq.})$$

Using the values given in the 1935 table of the International Committee on Atomic Weights (3), C = 12.00, H = 1.0078, and O = 16.0000, one obtains for the molecular weights of C_6H_{14}, CO_2, and H_2O, the values 86.109, 44.000, and 18.0156, respectively. In the past few years, however, a great deal of evidence has accumulated (2, 3) which indicates that the true atomic weight of carbon is somewhere between 12.007 and 12.009, and that of hydrogen is 1.0081. Using 12.007 and 1.0081, one obtains for the molecular weights listed above the respective values, 86.155, 44.007, and 18.0162. The change in the molecular weight of C_6H_{14} is 0.054 per cent, that in CO_2 is 0.016 per cent, and in H_2O 0.003 per cent.

It is obvious, therefore, that in this particular problem the substance whose mass should determine the amount of reaction in moles is, in order of preference, H_2O, CO_2, and C_6H_{14}, assuming, of course, that the true mass in grams of each substance is capable of being determined with about the same accuracy.

Another point which must be carefully considered, also, is that the determination of the amount of reaction from the mass of one substance, rather than that of another, may make permissible a greater amount of impurity in one of the reacting substances. An example of this situation is the combustion in oxygen of liquid ethyl alcohol. In such a case it would be unwise to determine the amount of reaction from the mass of ethyl alcohol without first establishing beyond doubt that the sample contained no water, whereas, the determination of the amount of reaction from the mass of carbon dioxide produced would make permissible the presence, in the ethyl alcohol, of a relatively large amount of water without introducing a significant error in the thermochemical value.

In general, it may be said that the "determining" substance should be one whose true mass can be accurately and readily measured. For example, carbon dioxide can be absorbed in ascarite (sodium hydroxide on asbestos) and water in anhydrous magnesium perchlorate (30, 31, 32). It should be emphasized that "weights in air" have no place whatever in accurate thermochemical work, because in chemical thermodynamics one must deal as accurately as possible in terms of moles, which can be derived only from true masses in grams. Where the substance determining the amount of reaction is absorbed in tubes to be weighed, the accuracy of the correction from apparent mass to true mass can be considerably increased by weighing the tube filled with hydrogen gas instead of the heavier oxygen, air, or nitrogen (30, 31, 32).

XII. CORRECTIONS TO STANDARD STATES

It frequently happens that the reactants and products of the chemical reaction as it takes place in the calorimeter are not in the accepted standard states. For this reason, it is imperative that significant data be recorded as to the phase, pressure, temperature, and concentration of the substances at the beginning and at the end of the reaction, so that the conversion to the standard states may be accurately made.

A study of each reaction will indicate with what significance the various properties must be recorded. In reactions involving aqueous solutions of strong electrolytes, for example, it is sometimes necessary to record the temperature to within 0.01°C., and similarly accurate information must be given as to the concentration. Absence of such information has made useless many thermochemical data obtained in the past.

The increasing accuracy and precision of thermochemical measurements has resulted in increasing the significance of information concerning the exact thermodynamic state of each substance participating in the chemical reaction. In former years, for example, the observed value of the heat evolved in the bomb calorimeter was taken as $-\Delta E$, the decrease in internal or intrinsic energy, for the pure reaction at 1 atmosphere. Several years ago, Washburn (45) investigated in considerable detail the reaction that actually occurs in the bomb calorimeter and showed that the value observed for the bomb reaction differs from $-\Delta E$ for the pure reaction at 1 atmosphere by amounts ranging from several hundredths to nearly 1 per cent.

That the reaction which actually takes place in the bomb calorimeter is a complex one is made evident by considering just what the initial and final states are. The following equation illustrates the nature of the bomb process for the combustion of benzoic acid when, as is usually done, a small amount of water is initially placed in the bomb;[13] the temperature and pressure of the initial state, T_A and P_A, usually will have values between 20° and 30°C., and between 30 and 40 atmospheres, respectively; the temperature and pressure of the final state will be $T_A + \Delta T$ and $P_A - \Delta P$, where ΔT will usually have a value from 1° to 4°C. and ΔP will usually be of the order of several atmospheres:

$$\begin{gathered}\mathrm{C_7H_6O_2(c)} + [(30 - a)\mathrm{O_2} + b\mathrm{H_2O}]\ (\mathrm{gas}) + [(\tfrac{1}{18} - b)\mathrm{H_2O} + a\mathrm{O_2}]\ (\mathrm{liq.}) = \\ [(7 - f)\mathrm{CO_2} + (\tfrac{45}{2} - d)\mathrm{O_2} + e\mathrm{H_2O}]\ (\mathrm{gas}) + [(3 + \tfrac{1}{18} - e)\mathrm{H_2O} + \\ d\mathrm{O_2} + f\mathrm{CO_2}]\ (\mathrm{liq.})\end{gathered}$$

This complex actual reaction is to be compared with the simple reaction for which the thermochemical value is desired, the temperature and pressure of the reactants and products being, for example, 25°C. and 1 atmosphere:

$$\mathrm{C_7H_6O_2(c)} + \tfrac{15}{2}\mathrm{O_2(gas)} = 7\mathrm{CO_2(gas)} + 3\mathrm{H_2O(liq.)}$$

To obtain the required thermochemical value for the simple reaction at 1 atmosphere, the observed value for the bomb reaction must be corrected with regard to the changes in internal energy with pressure of the initial oxygen and of the mixture of oxygen and carbon dioxide of the final state, the heat of solution of oxygen and carbon dioxide in water, and the heat of vaporization of water.

In a comprehensive study, Washburn (45) derived the complete and the approximate equations for correcting the heat of the bomb reaction to give

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[13] The presence of nitrogen in the oxygen used for the combustion further complicates the reaction through the formation of a significant amount of aqueous nitric acid:

$$\tfrac{1}{2}\mathrm{N_2(gas)} + \tfrac{5}{4}\mathrm{O_2(gas)} + \tfrac{1}{2}\mathrm{H_2O(liq.)} = \mathrm{HNO_3(aq.)}$$

the heat of the pure reaction at 1 atmosphere, and proposed certain standard states for bringing uniformity in the data of bomb calorimetry. The important variables in this connection are the volume of the bomb, the mass of substance burned, the amount of water initially placed in the bomb, and the initial pressure. Washburn's recommendations concerning the standard conditions of the bomb process, and his equations for correcting ΔE of the bomb reaction to ΔE of the simple reaction at 1 atmosphere, have been accepted by the Commission Permanente de Thermochimie de la Union Internationale de Chimie (24).

In the case of the combustion of organic compounds containing sulfur or a halogen, the reaction is even more complicated than that described above. In each such combustion involving sulfur or a halogen, the investigator must determine, with an accuracy commensurable in significance with his calorimetric accuracy, just what the actual reaction is that occurs in the bomb. The observed heat effect must then be corrected by the appropriate amount necessary to give the heat of a reaction in which all the reactants and products are in definite known states (4, 14).

XIII. THE "PRECISION ERROR" AND THE ESTIMATED UNCERTAINTY OF THE FINAL EXPERIMENTAL VALUE

For the proper comparison, with respect to precision, of the values obtained at various laboratories for the thermochemical constants, it is necessary that the "precision error" assigned to the various values be determined in a uniform manner. This uniform comparison will, however, be concerned only with the precision of the various sets of data and not with their actual accuracy, because the accuracy will depend upon the magnitude of the unknown or unaccounted-for systematic errors, the control of which is the burden of the individual investigators.

Serious systematic errors may arise from the determination of the electrical energy equivalent of the calorimeter, from an impurity in the reaction, or from the determination of the amount of reaction; and it is the duty of each experimenter to investigate thoroughly his apparatus, reaction, and procedure with regard to these possible systematic errors.

For determining in a formal and uniform manner the "precision error" to be assigned to the values obtained by various investigators for a given thermochemical constant, the following procedure is proposed:

Case I. Where the investigator determines the energy equivalent of his calorimeter directly with electrical energy.

1. The experimenter performs m acceptable experiments to determine the energy equivalent of the calorimeter directly in terms of electrical energy. The m values so obtained are averaged arithmetically, and the

deviation of each of the m values from the mean is recorded. Then the "energy equivalent error" is

$$a = \pm(100)\frac{2\sqrt{\Sigma\Delta^2/m(m-1)}}{(\text{value of energy equivalent})}\text{ per cent}$$

where $\Sigma\Delta^2$ is the sum of the squares of the m deviations.

2. The experimenter performs n acceptable experiments to determine the heat of a unit amount of the given reaction. The n values so obtained are averaged arithmetically, and the deviation of each of the n values from the mean is recorded. Then the "reaction error" is

$$b = \pm(100)\frac{2\sqrt{\Sigma\Delta^2/n(n-1)}}{(\text{value of reaction energy})}\text{ per cent}$$

3. The final assigned "precision error" of the average value obtained by the investigator for the heat of the given reaction is

$$\text{"precision error"} = \pm\sqrt{a^2 + b^2}\text{ per cent}$$

Case II. Where the investigator determines the energy equivalent of the calorimeter by means of a "standard" or "calibration" reaction.

1. The thermochemical value of the "standard" or "calibration" reaction, which has been accurately measured in one of the standardizing laboratories, has an "assigned error" equal to $\pm e$ per cent.

2. The experimenter performs m acceptable "calibration" experiments with the "standard" reaction to determine the energy equivalent of the calorimeter. The m values so obtained are averaged arithmetically, and the deviation of each of the m values from the mean is recorded. Then the "calibration error" is

$$c = \pm(100)\frac{2\sqrt{\Sigma\Delta^2/m(m-1)}}{(\text{value of energy equivalent})}\text{ per cent}$$

3. The experimenter performs n acceptable "reaction" experiments to determine the heat of a unit amount of the given reaction. The n values so obtained are averaged arithmetically, and the deviation of each of the n values from the mean is recorded. Then the "reaction error" is

$$b = \pm(100)\frac{2\sqrt{\Sigma\Delta^2/n(n-1)}}{(\text{value of reaction energy})}\text{ per cent}$$

4. The final assigned "precision error" of the average value obtained by the investigator for the heat of the given reaction is

$$\text{"precision error"} = \pm\sqrt{e^2 + c^2 + b^2}\text{ per cent}$$

In connection with the foregoing proposed procedure, the following points should be noted: The "error" of the average value of n experiments made to determine a given quantity is $\pm 2\sqrt{\Sigma\Delta^2/n(n-1)}$. This formula yields a value of the "error" within whose limits the "true" value has a chance of about 21 to 1 of being. The foregoing "error" is three times as large as the usual "probable error" computed with the formula $\pm 0.67\sqrt{\Sigma\Delta^2/n(n-1)}$, which indicates a chance of 1 to 1 that the "true" value lies within the given limits. The use of the "21 to 1" formula, rather than the "1 to 1," seems better because it yields an "error" which is conservative and reasonable. When the number of experiments is in the range of about five to seven, the "error" so computed has usually about the same magnitude as the average deviation. The deliberate performance of a very large number of experiments in order to reduce the value of the computed "error," when the average deviation remains unchanged, should be avoided, because the resulting "error" may then be so small as to be comparable with a number of possible small systematic errors and would consequently lose real significance. In order to prevent the occurrence of this misleading situation, it is recommended that not more than twelve experiments be made in any one series. It is also recommended that not less than four or five experiments be performed in any one series, because the performance of a lesser number will decrease the certainty attainable with a given apparatus out of proportion to its possibilities. Acceptable experiments include all except those in which a mistake or gross error has obviously been made.

In addition to the foregoing "precision error," which is calculable in a uniform manner from the data of various investigators, it is also desirable to assign an "accuracy error" or estimated uncertainty to the final value. This may be done by assigning a reasonable value to the one or more possible but unaccounted-for systematic errors, say $\pm f$ per cent, and combining it with the "precision error" by taking the square root of the sum of the squares. The "accuracy error" for cases I and II above would then be, respectively, $\pm\sqrt{a^2+b^2+f^2}$ and $\pm\sqrt{e^2+c^2+b^2+f^2}$, which should indicate the limits within which there would be a reasonable certainty that the actual true value of the thermochemical constant lies.

XIV. CONCLUSION

The contributions to thermochemistry which have been made in the United States in the past decade have been reviewed in the Annual Survey of American Chemistry (1), and most of the important modern thermochemical researches in both Europe and America have been reviewed in several articles by Roth (35, 36).

It is the opinion of the writer that the amount of work in thermochemistry that is being carried on in the laboratories of the world is entirely inadequate in view of its present-day importance to science. Thermochemical research is a field in which careful experimental work will not only yield important data for chemical thermodynamics, but will also produce data which can be utilized in conjunction with appropriate other values to obtain much needed information concerning the energies of formation of polyatomic molecules from atoms.

While it is true that research in thermochemistry has increased considerably in the past ten years, there is urgent need for more progress and expansion. It may be pointed out that even today there are a large number of chemical reactions for whose heats we depend upon the relatively uncertain data obtained nearly half a century ago. Some of these reactions are so important to both science and industry that the situation may be termed amazing.

Because the data of thermochemistry are of great importance to all branches of chemistry, to the theorists who are advancing our knowledge of molecular structure, and to all those industries whose processes are governed and controlled by the calculations and methods of thermodynamics, it is extremely desirable that every encouragement be given to thermochemical research, whether it be in the national standardizing laboratories, in the universities, or in the industrial laboratories, each of which will have its own particular part to play in the development of this important field.

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DISCUSSION

DR. MACINNES: Has any account been taken of the slight difference between the value of the faraday obtained from the silver coulometer and that found with the iodine coulometer by Washburn and Bates and by Bates and Vinal?

DR. ROSSINI: The present "best" value for the Faraday constant is based primarily upon the data from the silver coulometer (see Birge: ref. 6).

THE THIRD LAW OF THERMODYNAMICS

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The developments of modern theory and experiment in the field of the third law of thermodynamics have been of a character originally difficult to foresee. During the course of them many shifts in emphasis of particular phases of the subject have, of course, occurred. It remains true, however, that the ideas brought forth in the first few years following its announcement have given rise to more or less continuous discussion, extending into the last decade, and can scarcely be neglected in any summary of the present situation. They may be outlined in historical sequence somewhat as follows:

EARLY DEVELOPMENTS

1. In 1906 Nernst published his famous "heat theorem" as the consummation of the long-cherished ambition of the chemist to determine affinities from purely thermal data. The essence of the theorem and the most general of the early statements of it is that the entropy change accompanying a change in state approaches zero as the absolute zero of temperature is approached. More briefly (and less precisely)

$$\Delta S_0 = 0 \tag{1}$$

2. Originally the theorem was restricted to condensed systems. For the treatment of systems involving gases Nernst in 1908 invented his "chemical constants."

3. Nernst next, in 1910, in searching for a form of statement resembling the empirical ones for the first and second laws, adopted the "principle of the unattainability of the absolute zero."

4. About this time, Planck proposed and began the statistical interpretation of the concept of absolute entropy, leading to the formulation of the third law in terms of the entropy of individual phases as

$$S_0 = 0 \tag{2}$$

5. In 1912 we find the question of the entropy of supercooled liquids and solid solutions being debated. Nernst believed that phases of these types

might be included with the crystalline, and assigned zero entropy, while Planck and Einstein held that solid solutions at least should be assigned positive entropy.

6. In 1913 Polányi recognized that the effect upon entropy of increasing pressure should be much the same as that of decreasing temperature and that entropy changes at finite temperatures probably approach zero at infinite pressure.

7. Finally, beginning about 1913, the questions of "gas degeneracy" and the statistical calculation of the entropy constants were developed by various authors, bringing gases within the scope of the law in a broad sense.

RECENT DISAGREEMENTS OF OPINION

As so often happens, the underlying stimulus throughout these developments was provided not only by their importance but in no small part also by their controversial nature. It is, however, surprising to find to what extent this controversial element in the form of varying opinion as to validity and utility of the ideas, and differences in interpretation and usage, has persisted to the present time.

In illustration, divergent views from two recent treatments of the subject will be quoted. In 1930, Simon (44) concludes his very able monograph with these words: "*the Nernst Heat Theorem is a generally valid principle, which may properly be called the Third Law of Thermodynamics.*" In 1932, Fowler and Sterne (10), in their discussion of statistical mechanics applied to the calculation of entropies, make the following summarizing statement: "We reach therefore the rather ruthless conclusion that *Nernst's Heat Theorem strictly applied may or may not be true, but is always irrelevant and useless—applied to 'ideal solid states' at the absolute zero which are physically useful concepts the theorem though often true is sometimes false, and failing in generality must be rejected altogether.*"

Examination of the contexts of the above extracts lessens the sharpness of their divergence. Even allowing for this, a real difference remains, and the same is true among other authors in several important questions of interpretation, although in any practical sense there is general agreement and understanding.

OBJECTIVES IN THIS REVIEW

It is the purpose of the ensuing discussion to show the present status of the third law in its various ramifications, particularly as affected by the work of the last ten or twelve years. The experimental situation will be summarized, and each of the seven topics of the first section will be touched upon, in greater or less detail, in an order dictated mainly by convenience. Thus, since the chemical constants and the absolute entropies are much used in recording results, these will be briefly touched on in the beginning. Some ideas important to the understanding of certain experimental effects will next be taken up. The experimental material, followed by a discussion of its interpretation, will then be presented, together with some further points respecting usage.

CONCERNING CHEMICAL CONSTANTS

The short-comings of the chemical constants have been pointed out by Lewis and Randall (34). Most serious of these, perhaps, is the fact that they treat of an unnecessarily restricted phase of the question. In addition they introduce distasteful procedures of an empirical character which have often been badly handled, and they permit a certain adjustment between auxiliary constants which may obscure the degree of agreement in comparisons of them. These disadvantages are not sufficiently offset by slight gains in convenience in certain limited connections. In spite of this their use continues in the traditional manner by many authors. A very desirable simplification and unification would be introduced if their use were discontinued in favor of the better methods of treating the important thermodynamic properties of gases that have long been known and used. Definite progress in this direction, but not as much as might have been hoped for, can be reported. Numerical values of these constants will not be cited in this work.

ABSOLUTE AND RELATIVE ENTROPY IN THERMODYNAMICS AND QUANTUM STATISTICS

The proposal by Planck of the idea of absolute entropy initiated a long-continued discussion of its validity and usefulness.

Thermodynamically, of course, entropy is defined only to a constant, and entropy changes are therefore the only quantities necessary or significant for purely thermodynamic purposes. The third law in the form of equation 1 strictly requires only that the entropy of the phases to which it applies approach a common value at absolute zero. Planck's contribution, as far as thermodynamics alone is concerned, consists in the recognition that zero is the most natural choice of this common limit, though only questions of convenience can be involved.

Statistically, Planck (38) ultimately reached the conclusion that the entropy is given by

$$S = k \ln W \tag{3}$$

where W represents the number of detailed states or configurations in which a system of fixed energy may exist. With the contributions of modern theory as to what constitutes distinguishable states, it has been shown by various authors (33, 42) and is generally agreed that this equation does in fact bring the thermodynamic and statistical concepts of entropy into correct relationship. The question of the undetermined additive constant is again unsettled in a rigorous sense (9), but the assumption of any value for it other than zero is forced indeed. One may therefore always, though he need never, assume it to be zero. In the absence of significance of any other assumption, and in view of the simplicity and value of the physical picture and the unquestioned practical convenience so obtained, it appears an excess of conservatism not to make this extension of the entropy concept.

In using absolute entropies it is always recognized of course that the assumed zero of the scale may be subject to modification with advancing knowledge. It may often also prove convenient to adopt a reference scale which will not include certain factors which remain unchanged before and after all reactions of common interest. This is in fact being done at the present time when "practical" entropies are tabulated which do not include certain known effects.

QUANTUM STATISTICAL INTERPRETATION OF THE THIRD LAW

A system consisting of N similar particles cooled to the neighborhood of the absolute zero under conditions which permit the attainment of stable equilibrium at all stages will ultimately reach a condition in which all particles, and the system as a whole, are in the lowest energy level. If in this condition a single state or configuration of the system is represented, the entropy will be zero in accordance with equation 3.

If, however, two or more physically different states of identical energy of the particles are possible, W of equation 3 will no longer be equal to unity, nor the entropy to zero. If the number of states of equal energy accessible to the particles, or their "degeneracy,"[1] is represented by g, the number of distributions of the particles between these states will be g^N, and the entropy by equation 3 is $Nk \ln g$, or per mole

$$S = R \ln g \tag{4}$$

The question of the validity of the third law resolves itself therefore in such cases into the question of the singleness or degeneracy of the lowest energy state of the particles.

Again, if the system be composed of N particles of two or more kinds, of mole fractions X_1, X_2, etc., physically different states in number equal to $N!/(X_1N)!(X_2N)!\ldots$ may be formed by permutation of the unlike particles.

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[1] It is unfortunate that degeneracy as here used is diametrically opposed in significance to the phenomenon of gas degeneracy, which implies a loss of multiplicity. In spite of the opportunity for confusion the traditional usage will be followed.

If near the absolute zero these configurations all have identical energy, W in equation 3 for the system in the state of lowest energy is given by this expression. With the aid of Stirling's theorem we then find

$$S = -R\Sigma X \ln X \qquad (5)$$

This is the much discussed "entropy of mixing" which should be shown by solid solutions at the absolute zero.

With these preliminary statements for reference during the comparisons, the experimental results thus far available will next be presented in summarized form, after which the above points will be returned to and in part amplified.

EXPERIMENTAL STATUS OF THE THIRD LAW

In presenting the experimental material we shall make use of the previous summaries of Simon (44), adding to them any significant data of more recent date. (Sources will in general not be cited unless they cannot be traced through reference 44.)

1. Direct determinations of entropy changes at low temperatures

There is a considerable group of phenomena by which the demands of equation 1 may be directly checked by observations of various temperature coefficients at low temperatures. These coefficients are all related to the entropy changes in the corresponding changes in state and should approach zero at absolute zero if the third law in the form of equation 1 is valid. In all cases they appear to do so, and afford important confirmation of the law in very diverse applications.

Thus the coefficient of thermal expansion has been studied for a number of substances down to temperatures sufficiently low to indicate its zero value at absolute zero. Substances studied include, for example, aluminum (5), diamond, sodium chloride (5), silicon dioxide (5), calcium fluoride, FeS_2, and Pyrex glass (5) to liquid air temperatures, and silver, copper, and Jena glass to liquid hydrogen temperatures.

The temperature coefficient of magnetic susceptibility for paramagnetic and diamagnetic substances and the spontaneous magnetization of ferromagnetic substances also obey the demands of the law. The paramagnetic substances are particularly interesting in this connection, since the temperature at which the coefficients become zero varies widely. It is already reached at room temperature in some of the metals. It persists in certain salts to very low temperatures, becoming zero at liquid helium temperature for some of these but following approximately Curie's law at these temperatures for others. The latter are the substances now being employed for the production of very low temperatures. At sufficiently low temperatures even these will undoubtedly approach zero values.

Two other effects differing widely from the above and from each other, namely the temperature coefficient of electrical polarization in dielectrics and the thermoelectric power of metals, approach zero values with the temperature. They also therefore afford interesting confirmation of the law.

The one substance, helium, that remains liquid to the lowest temperatures studied, permits several interesting tests. Thus the surface tension and density of the liquid, and the equilibrium pressure for the crystal–liquid transition all approach temperature invariance as demanded by the theorem.

2. *Gas degeneracy*

We shall depart temporarily from the consideration of experimental data to mention the case of gas degeneracy, since it is analogous to the foregoing examples in that it requires a zero value of the pressure–temperature coefficient of gases at constant volume as the temperature approaches zero. The theory is now established and shows that for a gas obeying Bose-Einstein statistics the pressure should approach zero tangentially and for one following Fermi-Dirac statistics the pressure should approach a finite value but again with zero slope. Simon (44) gives an interesting discussion of the possibilities for experimental verification of such a tendency, and its recognition in other related phenomena. These lie on the border of the practicable at the present, but appear to offer definite hope of results in the future. The results in qualitative accord with theory obtained by treating electrons in metals as degenerate (whether one chooses to call them "gaseous" or not) should also be mentioned.

3. *Entropies of transition of crystals*

Of the reactions which cannot be directly studied at low temperatures, the crystallographic transitions, because of the small number of necessary experimental measurements involved, were among the first to receive attention. The earlier determinations include the rhombic–monoclinic sulfur, white tin–gray tin, quartz–cristobalite, and calcite–aragonite transitions. The accuracy of the measurements is not high in most of these cases. It is best for the tin transition, which offers satisfactory agreement with the theorem. This appears to be true of the other cases also to the extent that differences from zero of the entropy change at absolute zero as large as $R \ln 2$ (compare equation 4) are precluded.

To this older list may be added the two forms of cyclohexanol (28). Also, new determinations of heat capacities of rhombic and monoclinic sulfur (as yet unpublished) have recently been completed in this laboratory by McGavock, bringing this classic case into the group of accurate checks of the law.

4. *Crystal–liquid transitions*

Liquid helium at the absolute zero, as mentioned above, appears to have zero entropy. All others that have been studied exist at low temperatures in the supercooled condition. These "glasses" without exception show positive entropies in varying amount at absolute zero. The most thoroughly investigated case is that of glycerol glass, for which the molal entropy at 0°K. appears to be 4.6 E.U. The corresponding entropy of ethyl alcohol glass is about 2.6 E.U. For quartz glass the value is about 1 E.U. Other less completely investigated substances show similar effects.

5. *Entropy of solutions*

A complete investigation of a glassy solution of glycerol and water, in which specific heats were measured down to 9°K., was made by Simon. The reaction studied may be written, per "mole" of the final solution,

$$0.470C_3H_5(OH)_3 \cdot 0.032H_2O(\text{liq. sol.}) + 0.498H_2O(\text{ice}) = 0.470C_3H_5(OH)_3 \cdot 0.530H_2O(\text{liq. sol.})$$

The measured value of ΔS for this reaction at 273°K. was 3.55 cal. per degree. In conjunction with the specific heat data, this gave as the difference in entropy of the two solutions at 0°K. 1.30 ± 0.36 cal. per degree. The value of this difference calculated by equation 5 is 1.14 cal. per degree.

Earlier investigations by Gibson, Parks, and Latimer on mixtures of ethyl and propyl alcohols showed that to liquid air temperatures at least the heat capacity of the glassy solution is approximately an additive function of those of the pure glasses, indicating a positive entropy for the solution at absolute zero.

Of crystalline solutions only one system has been experimentally investigated. Eastman and Milner (7) found for the reaction

$$0.728AgBr(\text{cryst.}) + 0.272AgCl(\text{cryst.}) = 0.728AgBr \cdot 0.272AgCl(\text{cryst. solution})$$

that ΔS at 298°K. is 1.12 ± 0.1 cal. per degree, as compared with the calculated value (equation 5) 1.16. From the specific heat data the value found for the absolute zero was 1.03, within the error therefore unchanged from the above. In view of the simple specific heat laws obtaining for crystals, extrapolation to the absolute zero involves less uncertainty than usual. This example offers, therefore, particularly strong confirmation of the belief that the entropy of mixing is present in all such phases at the absolute zero.

6. *Entropy changes in chemical reactions*

Numerous reactions of varied types, including heterogeneous reactions involving crystals only, and heterogeneous and homogeneous gas reactions, have been studied from the standpoint of the third law. High accuracy is in general difficult of attainment, because independent determinations of changes in heat content and free energy and the individual heat capacities of all reactants and products are often necessary, and because the exact identity of the solid phases in the various measurements cannot always be assured. When the entropy change can be directly determined from temperature coefficients of electromotive force, as is often possible, the uncertainties are greatly reduced.

Concerning the reactions in condensed systems, it may be said that in all cases the third law is verified within the error of measurement. In a majority of them the error is sufficiently small to make entropy changes at absolute zero of the order of $R \ln 2$ extremely improbable, and in perhaps a half dozen of the reactions the law is substantiated within 0.2 or 0.3 E.U.

In the gas reactions, which comprise a larger and more important group, a similar statement may be made, with a few exceptions where apparent disagreement occurs. As the comparison of individual entropies of the gases, to be discussed below, is a more decisive test of the law, and since the reactions for which disagreements are most apparent involve substances which also show the effect individually, no list of the numerous reactions studied will be given here, and the discussion of the apparent anomalies will be deferred. Compilations of data may be found in the summaries by Simon (44).

It should be mentioned also that many reactions used by Latimer and his associates in estimation of entropies of ions constitute checks, often of high accuracy, of the third law. These reactions have been conveniently tabulated by Latimer, Schutz, and Hicks (30).

7. *Comparison of entropies of gases calculated quantum-statistically with values derived by application of the third law*

The important contributions of wave mechanics to the older quantum-statistical theory are: the unambiguousd efinition of W in equation 3 as the number of (linearly independent) wave functions necessary for the representation of the possible states of a system; the correct assignment of the multiplicity of degenerate rotational states, and electronic and nuclear spin multiplicities; the justification and explanation of "symmetry numbers" in treatment of rotational states; the recognition of the non-combining ortho and para forms of molecules containing two (or more) similar atoms having a nuclear spin; and the proof that nuclear spin entropies cancel in reactions at ordinary and high temperatures, making possible the assignment of "practical entropies" neglecting them.

The classical calculations of the entropy constants of monatomic gases fortuitously were first applied to substances of no electronic degeneracy.

The agreement obtained with the experimental (third law) values was therefore satisfactory. For such vapors as the alkali metals and the monatomic halogens and others the multiplicity of the lowest electronic level contributes to the entropy. When this is taken into account, as determined spectroscopically, agreement is found throughout between the calculated and third law values within the error of measurement, which is in general small. The list of elements studied to date includes: helium (25), neon, argon, krypton (27), sodium, potassium, copper, silver, gold, zinc, cadmium, mercury, carbon, lead, tungsten, chlorine, bromine, iodine. The data in the literature are often compared in the form of the chemical constants, and will not be given in detail here.

In diatomic and polyatomic gases any of the factors mentioned in the opening paragraph of this section may be of importance in particular instances. A summary of entropies obtained by the application of the third law and by statistical calculation on the basis of spectroscopic evidence is presented in tables 1 and 2. The spectroscopic entropies do not include nuclear spin terms and are therefore the practical values. The temperature of comparison is 298.1°K., except for nitric oxide, where it is 121.36°K. The accuracy of the calorimetric measurements in table 1 is in all cases high, errors being of the order of 0.1 E.U. throughout.

TABLE 1

Molal entropy of gases

SUBSTANCE	ENTROPY (CALORIMETRIC)	ENTROPY (SPECTROSCOPIC)	REFERENCES
H_2	29.7	31.23	(11, 16)
N_2	45.9	45.788	(15)
O_2	49.1	49.03	(17)
HCl	44.5	44.64	(19)
HBr	47.6	47.48	(20)
HI	49.5	49.4	(21)
CO	46.2	47.316	(6)
NO	43.0	43.75	(23)
H_2O	44.23	45.17	(13)
N_2O	51.44	52.581	(3)

For a number of gaseous substances not included in table 1 calorimetric entropies of less accuracy or completeness in certain phases may be compared with statistical values. These are listed in table 2. For bromine and iodine the calorimetric entropy of the liquid and solid, taken from the compilation of Kelley (29), has been supplemented for the purpose of this comparison by vaporization entropies obtained from Lewis and Randall (34). It should be said that Giauque (12) has shown that the spectroscopic calculation confirms the calorimetric entropy of solid iodine within 0.1 E.U. Much of the discrepancy shown in the table is in this case therefore connected with the entropy of vaporization. This is probably also true of the other halogens. Pending the appearance of more accurate investigations of several of the substances in the table, little weight can be given the calorimetric entropies for third law comparisons.

In the figures for hydrogen, deuterium, carbon monoxide, nitric oxide, nitrous oxide, and water, tables 1 and 2 contain the only examples now known of crystalline systems of "one component" which appear to deviate from the third law by amounts definitely larger than the experimental error. These discrepancies are however explainable along lines discussed later.

The close agreement, taking into account the explanation of the "exceptions," of the calorimetric and spectroscopic entropies shown in table 1 constitutes perhaps the most accurate and convincing proof of the validity of the third law provided by any one method of testing it. At the same time the possibility of applying spectroscopic data to the calculation of entropy, which affords this excellent substantiation of the law, constitutes a direct threat to its future usefulness. Thus, there is little point in the purely calorimetric determination of affinity if it can be done with greater accuracy and convenience by other methods. The spectroscopic method is unquestionably capable of great extension and is destined to take a predominant part in future determinations of entropies. On the other hand, there will always be many substances which will not be susceptible of this treatment, and for them the calorimetric method will retain its importance.

TABLE 2

Molal entropy of gases

SUBSTANCE	ENTROPY (CALORIMETRIC)	ENTROPY (SPECTROSCOPIC)	REFERENCES
D_2	33.65	34.36	(8, 24)
Cl_2	52.8 ± 0.4	53.310	(18, 29)
Br_2	59.5	58.667	(19, 22)
I_2	63.1	62.29	(12, 19)
CO_2	52.4	51.07	(1, 19, 26)
NH_3	47.2 ± 1.0	46.4	(14, 19)
CH_4	44.3	44.35	(14)

Moreover, even in those cases where more accurate and convenient methods can be applied, the comparison with third law entropies permits interesting conclusions concerning phenomena occurring in the crystals. The "exceptions" cited above are examples of this, since for some of them the comparisons suggested conditions within the crystals (see below) which might otherwise not have been brought to light. In other cases, for example, hydrogen (and the hydrogen halides and others), the question of the presence or absence of molecular rotation within the crystal has been answered by comparisons of this kind. Also the general agreement of the third law and the statistical values of the entropy when nuclear spin effects are neglected shows that the spin orientations in crystals are still indefinite at the lowest temperatures of measurement. As a further illustration of the value of low temperature heat capacity studies, the suggestion by Simon (44) of the possibility of deciding by means of them whether the rotational levels in crystalline hydrogen remain completely degenerate at very low temperatures, may be mentioned.

INTERPRETATION OF EXPERIMENTAL DATA

The data summarized in the last section may be interpreted in connection with equations 1 to 5 as follows.

In the great majority of the many cases involving pure crystalline substances equations 1 and 2 are found definitely to hold and the entropies at the absolute zero may be taken as zero. In conjunction with equations 3 and 4, and neglecting nuclear spin degeneracy, this means that in these crystals the states obtained by ordinary methods of cooling to very low temperatures are statistically single. (The possibility that multiplicity exists but is the same in all cases may be dismissed as unlikely.) In considering the experimental confirmation of the third law from this angle, Schottky (41) has suggested that even though a molecule possess an intrinsic degeneracy this is resolved by the crystalline forces. There is some evidence (44) for this in the work of Simon, Mendelssohn, and Ruheman (47) concerning the heat capacities of mixtures of ortho- and para-hydrogen at very low temperatures. A theoretical treatment of the degeneracy of vibrational levels in crystal lattices has been attempted by Ludloff (35), who applied quantum statistical methods to a simple model. His result was that multiplicity of a high order appears in certain "lattice terms," but that the lowest level (in his model) is single.

The experimental evidence that solid solutions must be assigned finite positive entropy at absolute zero is also definite. The amount of this entropy proves to be calculable by equation 5. The agreement with the formula is not detectably affected by the fact that in the real, as contrasted with the ideal, solid solutions all of the various exemplars do not have identical energies. We are, in the real cases, not dealing with as sharp or complete a degeneracy of the system. The manner of formation of these "frozen" phases, nevertheless, requires the inclusion of the same number of configurations in the definition of the macro-state as for the ideal unconstrained system. The statistical multiplicity is therefore the same in the two cases, and equation 5 equally applicable to the entropy. The quantum-mechanical aspects of this question will be mentioned later.

The interpretation of the entropy of glasses, at absolute zero, which has been seen also to be well established experimentally, is not so straightforward as for the solid solutions. It is no doubt to be associated with the existence of several quantum states of nearly equal energy of the molecules in the glass, due to slight differences in orientation or relative position. The molecules are therefore probably to be treated as possessing a degeneracy (again not sharp) and handled by means of equation 4. (See also in this connection the work of Pauling and Tolman (37).) The advance prediction of the value of g in this equation (better, perhaps, the average value computed from the total number of states possible for the system as a whole) is not, however, possible. Working backward from the observed entropies its "apparent" value (only integral values are strictly significant) is found to be about 10 for glycerol, 3.7 for ethyl alcohol, and 1.6 for quartz glass. We are again dealing in these examples with frozen phases, in which the constraints require the recognition of a large number of possible exemplars at absolute zero, and a statistical multiplicity.

The indefiniteness of state in glasses and solid solutions, and the corresponding entropy, is often associated with a randomness (34) or lack of order (44, 45) in distribution of molecules. Insofar as these terms are taken to imply a multiplicity of possible quantum states of nearly equal energies, as outlined above, there can be no objection to this usage. The words are, however, susceptible of interpretation as a geometrical complexity or irregularity of arrangement of molecules in a single state. Such complexity will in general be accompanied by increased possibilities for additional states, justifying the association of terms. In itself, however, this factor seems to have no necessary or demonstrable connection with entropy (cf. ref. 7, p. 454). The interesting example of liquid helium near the absolute zero mentioned above may constitute a case in point. Evidence is accumulating (46) which eventually may determine the nature of this state. It is conceivable that it will prove not to possess any perfect order. It is already demonstrated to have zero entropy. The important thing is, therefore, that a single quantum state is represented, regardless of the interest that may attach to the visualization of this state. Compare in this connection the suggestion of Rodebush (40).

Turning to the "exceptions" of tables 1 and 2, Giauque and his associates have proposed (3, 6, 23) explanations for three of them. In carbon monoxide, nitric oxide, and nitrous oxide, they assume the existence of nearly equivalent states producible by end-for-end rotational displacement of the molecules, and that under the condition of formation the crystal does not distinguish between these states. By assuming the predictable values of g in equation 4 one obtains entropies of the right magnitude. The explanation is therefore plausible.

For water, Pauling, in a note soon to appear, has proposed an indefiniteness in the position of certain hydrogen bonds in the crystal as a more probable explanation than the earlier suggestion of Giauque and Ashley (13) of rotating molecules in the crystal. The value of g in equation 4 predicted by either of these pictures is approximately correct in magnitude. Experimental decision between them seems possible and may be awaited with interest.

The resolution of the long standing discrepancy of hydrogen exhibited in table 1 became possible only with the advent of wave mechanics. "Normal" hydrogen crystals are now known to be a solid solution in the proportion of 1 to 3 molecules of the "para" and "ortho" forms resulting from opposed and parallel nuclear spins. The para molecules are not rotating and have no degeneracy. The ortho molecules do rotate in the crystal and have a combined rotational and spin degeneracy of 9. The entropy of such crystals is obtained therefore by combining the "degeneracy entropy," $S = \frac{3}{4} R \ln 9$ (equation 4) with the "permutation entropy," $S = -\frac{1}{4} R \ln \frac{1}{4} - \frac{3}{4} R \ln \frac{3}{4}$ (equation 5). The value 4.39 E.U. so obtained, added to the third law value, gives the correct absolute entropy of the gas, 33.98 E.U. To obtain the "practical entropy" given in table 1 the high temperature spin entropy, $R \ln 4$, is deducted. For full discussion of these points the work of Giauque (11, 16) and Fowler and Sterne (10) may be consulted. It is interesting that at helium temperatures, the hydrogen begins to dispose of some of the entropy corresponding to the above terms (44). The calorimetric entropy in table 1 is based on extrapolations from temperatures where this effect is not yet manifest.

Deuterium is the only isotope hitherto separated from the naturally occurring mixture and experimentally studied by third law methods. In a general way the state in normal deuterium crystals at low temperatures is analogous to that of normal hydrogen, though the proportions and multiplicities of the ortho and para forms are interestingly different. Taking these into account the experimental and statistical determinations of entropy are again in good agreement (8).

The natural occurrence of isotopic mixtures in many elements and their compounds introduces, in a strict sense, a multiplicity and entropy in their frozen crystals at low temperatures. These differ in no essential way from any other solutions, so far as third law considerations are concerned. Since the proportions of the mixtures do not change significantly in chemical reactions this effect need not be included in the practical entropies. In artificially prepared mixtures of comparable proportions of hydrogen and deuterium and their compounds, appreciable differences in mole fraction of the various molecular types may result in reactions. This may introduce slight effects in the mixing terms in third law calculations relating to such mixtures, which are however not of practical importance. It should be said that the purely statistical treatment of entropy effects in isotopic mixtures involves many interesting points concerning spin and rotational multiplicities and the occurrence or non-occurrence of ortho and para forms in the different molecular types. The examples of chlorine (18) and hydrogen–deuterium mixtures (24) may be cited. These effects are not directly connected with the third law and will not be discussed here.

The interpretation of the entropy of the "frozen" phases discussed above introduces, of course, a limitation of the third law as expressed by equations 1 and 2. It nevertheless appears to meet successfully and satisfactorily all thermodynamic and statistical requirements. Many authors (44), however, prefer to preserve the generality of these equations by excluding frozen phases from thermodynamic consideration. Their basis for this is that the constraints in these systems cannot be rigidly maintained. Ideally reversible isothermal processes involving them cannot therefore be carried out, and no significant entropy changes determined by such processes, because of shifts with time toward the stable states (44, 45).

It is true that complete thermodynamic equilibrium is not established in these phases. For their definition, not only the numbers and kinds of atoms and the energy and volume of the system, which ordinarily suffice, but some additional specification, such as the temperature or a statement of constraints, must also be included. Once this is done, and adhered to, thermodynamics may be successfully applied, and often is in many actual systems. The element of time, except as the uncertainty principle may be involved, then does not enter in any significant sense (32). It appears an unnecessary limitation to exclude such treatment completely from thermodynamics. These questions have been discussed at some length by Eastman and Milner (7), and need not now be further elaborated.

It remains, however, to mention the behavior predicted by wave mechanics for ideal solutions and constrained systems such as real solutions and glasses on cooling to temperatures approaching absolute zero. This subject has been discussed by Rodebush (40). Certain of his conclusions are criticized in a forthcoming note by Pauling and Eastman (36). The features of interest here may be outlined as follows. Consider first a solution which is ideal at all temperatures. If such a solution be cooled to the neighborhood of absolute zero so slowly that it remains for times long compared with the time of transition between configurations at each temperature, its entropy of mixing will be lost, owing to the splitting of levels resulting from interaction of the various configurations. This will also be true on rapid cooling, provided the solution is finally held for a long time (compared to the time for transitions) at the low temperature. If such times be not allowed, the degeneracy of the system will not be lost and the entropy of mixing will remain. In the constrained systems, however, these long times are inconsistent with the constraints and cannot be considered, since the systems would go over, if transitions are occurring between configurations, to stable ones of zero entropy. In all cases of physical interest (real solutions and glasses, and ordinary times of observation) therefore, the predictions are in harmony with those deduced above from the older statistical considerations. The application of quantum mechanics nevertheless represents a real advance in interpretation.

THE PRINCIPLE OF THE UNATTAINABILITY OF THE ABSOLUTE ZERO

The relation of the "principle of unattainability" to the Nernst theorem and to the second law is outlined by Bennewitz (2), and shown not to be identical with either. The adoption of the views outlined above recognizing the existence of non-zero entropies or entropy changes in certain cases near the absolute zero denies the purely thermodynamic implications of the unattainability principle. This does not impair the truth of the principle, but places its validity upon a different basis, namely, the impossibility of carrying out experimentally isothermal processes involving certain types of constrained systems near absolute zero. This impossibility is perhaps more nearly related to fact than principle. In this case the fact is, of course, readily interpretable (43). This does not detract from the value or correctness of the idealized thermodynamic consideration of such processes. Nor is it justifiable to consider solid solutions and glasses as "non-thermodynamic" (44) phases, since in certain real processes their constraints can be maintained, and thermodynamics is directly applicable.

It may be noted here also that the unattainability theorem cannot be connected with the uncertainty principle as suggested by Rodebush (40). The latter principle in fact requires (36) the assignment of non-zero values of entropy to glasses and solutions under the circumstances discussed above, and is thus directly opposed, thermodynamically, to the former.

Apart from these considerations, the use of the unattainability theorem is generally but a clumsy alternative for more straightforward methods, and little of value is ever gained from it alone. Eastman and Milner (7) have suggested that it may well be dispensed with in thermodynamics.

ENTROPY AT HIGH PRESSURES

This question was first approached by Polányi (39) and later developed independently by Lewis (31), the conclusion of both authors being that at infinite pressures entropy becomes zero at finite temperatures. Lewis showed that the experimental behavior of the alkali metals appears to be in harmony with this idea. Bridgman (4) has recently pointed out, as a condition for this behavior, that the coefficient of thermal expansion must ultimately decrease at least as rapidly as $1/p$. He finds that for substances other than the alkali metals this is far from true at the highest pressures yet reached experimentally. Recognizing that experimentally attainable pressures are relatively small in the sense implied in this connection, and that a reversal in trend at higher pressures may occur, he nevertheless questions the necessity for the assumption of approach to zero entropy, suggesting that degrees of freedom previously frozen may become active at high pressures. It is, however, difficult to believe that the effect of increasing pressure will not ultimately lead to increasing separation of the energy levels of any system, with consequent continued decrease toward unity in the number of statistical distributions consistent with the temperature, and therefore to zero entropy. If however this occurs only outside the range of pressures that can be studied experimentally, the usefulness of the theorem is of course reduced.

STATEMENT AND NATURE OF THE THIRD LAW

There is one statement of the third law which meets with nearly universal agreement. Any phase cooled to the neighborhood of the absolute zero under conditions such that unconstrained thermodynamic equilibrium is attained at all stages of the process, approaches a state of zero entropy. This is, however, an unnecessarily restrictive form, since many constrained systems also approach zero entropy. The various formulations which attempt to include this fact have been briefly discussed by Eastman and Milner (7), who also propose the following inclusive and sufficiently restrictive statement; the entropy at the absolute zero of any phase of sharply specifiable energy is zero. In view of the general understanding which prevails, matters of statement are perhaps unimportant, except in so far as they emphasize significant features.

The statement of the third law in the form that entropy is a finite positive quantity, together with the rule of its approach toward zero with decreasing temperature or increasing pressure (31, 34), emphasizes its distinction in character from the other two laws. Each of the latter defines a thermodynamic quantity, while the third law merely limits one of these quantities. It differs essentially in type therefore from the first and second laws. Since it does not add to the content of the science its incorporation as one of its "laws" is of doubtful logic, although this usage seems to be established.

CONCLUSION

The evidence and arguments presented (very sketchily, indeed) in this review amply substantiate the central theorem under discussion. Its accurate application will always require discretion in consideration of the factors discussed here, as well as numerous points of a practical character. Moreover, the appropriateness of the usually accepted name is questionable. In spite of this, it seems not too much to say that neither the validity of the third law, its great utility, nor its continued importance since its inception in determining the course of the related sciences, can reasonably be denied.

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DISCUSSION

Dr. Rodebush. I do not disagree in any important detail with what Dr. Eastman has said, but I should like to add a few words as to my point of view. Eastman and Milner have stated that the low temperature states of mixed crystals and supercooled liquids are statistically indeterminate. Lewis and Gibson used the term "randomness" in this connection. If we understand by randomness the possibility of the existence of different configurations having the same energy then we can interpret the situation, but not without recourse to wave mechanics. According to wave mechanics a system behaves as though it were aware of the existence of other configurations having the same energy as the one in which it exists. This leads to a multiplicity of energy levels. If a system were in the lowest of these energy levels its entropy would be zero, but we can not know which level it is in because of the uncertainty principle. To determine the energy exactly would require so long a time that the system might not remain in its original state. This point of view is, therefore, in entire agreement with the statement of Eastman and Milner, that the low temperature state is statistically undefined.

Dr. Johnston. I think it unfortunate in some respects that the concept of zero or minimum entropy is so closely associated with that of minimum energy or that entropy increases are ordinarily associated with temperature increases. The relation between entropy and energy is an indirect one and exists because increase of thermal energy results, in practice, in an increased distribution of molecules among a wide number of discrete states. But it is the distribution, rather than the energies involved, which is the important thing. Thus if one could activate a gram-atom of mercury vapor *all* to the metastable $^3P_0$ state there would be no increase in entropy in spite of this large addition of energy. The fact that the system produced does not correspond to a stable one has, of course, nothing to do with the immediate value of the entropy. When this conception is applied to the situation which exists at or near the absolute zero it is apparent that disagreements with respect to the validity of the third law resolve themselves into disagreements in arbitrary definition.

THE CALCULATION OF THERMODYNAMIC FUNCTIONS FROM SPECTROSCOPIC DATA[1]

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I. INTRODUCTION

Whenever all the energy levels of a system are known all its equilibrium properties may be calculated, including the heat capacity, heat content, entropy, and free energy with which this paper is concerned. The analysis of spectroscopic data is a powerful method of obtaining such energy levels, and within recent years this new thermodynamic tool has been developed rapidly. This review consists of three parts: the first sketches the fundamental theory, the second outlines the more important techniques of numerical calculation, and the third discusses the results that have been obtained by use of the method.

II. FUNDAMENTAL THEORY

Consider an assemblage of N identical systems of one kind and N' of a second kind, where both N and N' are very large numbers. Let the possible energy levels be ϵ_i and ϵ'_j, where i and j represent all the quantum numbers required to specify the condition of a system. Let the number of systems in the various states be N_i, N'_j. The quantum weight of the assemblage in this condition is the number of permutations

$$W = N!\,N'!\,\Big(\prod_i N_i!\Big)^{-1}\Big(\prod_j N'_j!\Big)^{-1} \tag{1}$$

or

$$\log W = N \log N - \sum_i N_i \log N_i + N' \log N' - \sum_j N'_j \log N'_j \tag{2}$$

The most probable state of the assemblage is determined by the conditions

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$$\left.\begin{aligned} -\delta \log W &= \sum_i (\log N_i + 1)\,\delta N_i + \sum_j (\log N'_j + 1)\,\delta N'_j = 0 \\ \delta E &= \sum_i \epsilon_i \delta N_i + \sum_j \epsilon'_j\, \delta N'_j = 0 \\ \delta N &= \sum_i \delta N_i = 0 \\ \delta N' &= \sum_j \delta N'_j = 0 \end{aligned}\right\} \tag{3}$$

from which, by Lagrange's method of multipliers,

$$\left.\begin{aligned} N_i/N &= e^{-\mu\epsilon_i}\Big(\sum_i e^{-\mu\epsilon_i}\Big)^{-1} \\ N'_j/N' &= e^{-\mu\epsilon'_j}\Big(\sum_j e^{-\mu\epsilon'_j}\Big)^{-1} \end{aligned}\right\} \tag{4}$$

Since appreciable deviations are easily shown to be very improbable, equations 4 are the equilibrium conditions. Then since μ is the same for two substances in equilibrium, it must be a kind of temperature.

In what follows only the unprimed systems are considered. Define

$$S = k \log (W/N!) \tag{5}$$

where k is an as yet undetermined constant. Since this S is an additive property of an assemblage which approaches a maximum as the assemblage approaches equilibrium adiabatically, it must be proportional to the thermodynamic entropy; then by suitable choice of k the two can be made equal.

Define

$$Q = \sum_i e^{-\mu\epsilon_i} \tag{6}$$

The total energy is then

$$E = -\,(N/Q)(\mathrm{d}Q/\mathrm{d}\mu) \tag{7}$$

A kind of specific heat is

$$\mathrm{d}E/\mathrm{d}\mu = (N/Q^2)(\mathrm{d}Q/\mathrm{d}\mu)^2 - (N/Q)(\mathrm{d}^2Q/\mathrm{d}\mu^2) \tag{8}$$

At equilibrium

$$S = Nk \log Q + \mu k E - k \log N! \tag{9}$$

from equations 4 and 5. Define

$$-\mu A = N \log Q - \log N! \tag{10}$$

It is clear from equation 9 that A has the properties of maximum work.

The equations 7 to 10 are a complete set and could be used in that form. It is customary, however, to replace the statistical "temperature," μ, by the thermodynamic temperature, T, defined by

$$1/T = \partial S/\partial E = (\partial S/\partial \mu)/(\partial E/\partial \mu) = \mu k \tag{11}$$

When T replaces μ in equation 4 the Maxwell-Boltzmann distribution law is obtained in its familiar form. When T is substituted in equations 7 to 10 the results are

$$\begin{aligned} E &= -Nk(Q'/Q) && (12)\\ C_v &= \mathrm{d}E/\mathrm{d}T = (Nk/T^2)[Q''/Q - (Q'/Q)^2] && (13)\\ -A/T &= Nk \log Q - k \log N! && (14)\\ S &= Nk[\log Q - (1/T)(Q'/Q)] - k \log N! && (15) \end{aligned}$$

It is evident from the form of the foregoing equations that when the energy of a system splits into several independent parts

$$\epsilon_i = \epsilon_j^{\mathrm{I}} + \epsilon_k^{\mathrm{II}} + \cdots \tag{16}$$

where no quantum number occurs in more than one subscript, then Q is a product of independent factors $Q^{\mathrm{I}}Q^{\mathrm{II}} \cdots$, and the thermodynamic functions are sums, for example $E = E^{\mathrm{I}} + E^{\mathrm{II}} + \cdots$. Now for any system in field-free space the wave equation may be separated to give

$$[\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 + (8\pi^2 m/h^2)W]\psi = 0 \tag{17}$$

for the motion of the center of gravity. When the system is confined to a cubical box of edge l the energy levels corresponding to equation 17 are

$$W = (h^2/8ml^2)(n_x^2 + n_y^2 + n_z^2),\ n_u = 0, 1, 2 \cdots \tag{18}$$

Each translational degree of freedom thus makes a separate contribution

$$Q = \sum_0^\infty e^{-n^2h^2/8ml^2kT} \tag{19}$$

or

$$\mathbf{Q} = (2\pi mkT/h^2)^{1/2}l + 1/2 \tag{19a}$$

the summation being made by the Euler-Maclaurin expansion formula and becoming asymptotically exact as $h^2/8ml^2kT \rightarrow 0$. Such asymptotic sums and all functions derived from them will be printed in bold-face type throughout this paper. The error in equation 19a as found by direct summation of equation 19 is 1 in 10^8 for $h^2/8ml^2kT = 1.4$ and 1 in 10^6 for $h^2/8ml^2kT = 0.7$. These values are far larger than any of experimental interest; for example, for H_2 at 1°K. with $l = 10^{-2}$ cm., $h^2/8ml^2kT = 10^{-10}$ and the error in equation 19a has become totally insignificant; even when the second term is dropped the error is only 1 in 10^5 in Q, corresponding to 0.00015 cal. per degree in S and rather less in C_v. When this very satisfactory approximation is made, three translational contributions give

$$\mathbf{E} = (3/2)NkT \tag{20}$$

$$\mathbf{C_v} = (3/2)Nk \tag{21}$$

$$\begin{aligned}\mathbf{S} &= Nk[\log (2\pi mk/h^2)^{3/2} + \log V + (3/2) \log T + 5/2 - \log N] \\ &= Nk[\log (2\pi m)^{3/2}k^{5/2}h^{-3} + (5/2) \log T - \log P + 5/2]\end{aligned} \tag{22}$$

$$-\mathbf{F}/T = -A/T - Nk = Nk[\log (2\pi m)^{3/2}k^{5/2}h^{-3} + (5/2) \log T - \log P] \tag{23}$$

$$\mathbf{H} = (5/2)NkT \tag{24}$$

$$\mathbf{C_p} = (5/2)Nk \tag{25}$$

Since the perfect gas law, $PV = NkT$, is used in obtaining equations 22 to 25, it may be well to point out that this law follows at once from equation 20, since for any distribution of velocities $PV = (2/3)E$. The constant k, however, must of course be determined experimentally from equation 21 or 25. When numerical values of the constants are used, the molar entropy and free energy at atmospheric pressure become

$$\mathbf{S} = (5R/2) \log T + (3R/2) \log M - 2.300 \tag{22a}$$

$$-\mathbf{F}/T = (5R/2) \log T + (3R/2) \log M - 7.267 \tag{23a}$$

where M is the molecular weight. This derivation of the Sackur-Tetrode equation is more satisfactory than any that were given before quantum mechanics was developed. It should be noted that the term $-k \log N!$ in equation 9 has been included in the translational contribution to S and $-F/T$; it is not to be used again when the internal energy contributions are evaluated.

III. THE TECHNIQUE OF NUMERICAL CALCULATIONS

The rotational sum for diatomic molecules

For all real molecules the translational energy is the only part that can be separated out as in equation 16. The rotation-vibration energy for a diatomic molecule is represented by some such expression as

$$E = E_0 + hc[\omega_0 v - x\omega_0 v^2 + y\omega_0 v^3 + \cdots] + hc\{B_v[J(J+1) + \text{const.}] + D_v J^2(J+1)^2 + \cdots\} \tag{26}$$

where

$$B_v = B_0 - \alpha v + \gamma v^2 + \cdots \tag{26a}$$

$$D_v = D_0 + \beta v + \cdots \tag{26b}$$

The problem of finding Q for an energy of the form in equation 26 is conveniently preceded by finding it for the rotational part

$$E_{\text{rot}} = hc[BJ(J+1) + DJ^2(J+1)^2 + FJ^3(J+1)^3 + \cdots] \tag{27}$$

where for convenience the subscripts v have been dropped.

The wave functions for a rigid rotator are

$$\psi = P_J^M(\cos\theta)e^{iM\varphi} \tag{28}$$

where P_J^M are the associated Legendre polynomials. The corresponding energy levels are

$$E = (h^2/8\pi^2 I)J(J+1) = hcBJ(J+1) \tag{29}$$

The quantum number J measures the total angular momentum and takes values 0, 1, 2 $\cdots$. The quantum number M is the projection of J on a preferred external direction, with allowed values $0, \pm 1, \pm 2 \cdots \pm J$. When there is no preferred direction (absence of external fields) the level J is degenerate with a quantum weight $2J + 1$. For such a rotator

$$Q = \sum_{J=0}^{\infty} (2J+1)\,\text{exp.}\,[-(hcB/kT)J(J+1)] \tag{30}$$

When hcB/kT is large, successive terms in equation 30 decrease rapidly, but when it is small direct summation becomes extremely laborious. It is then convenient to replace the sum by an asymptotic expansion[2]

$$\begin{aligned} Q &= e^{hcB/4kT}[kT/hcB + 1/12 + (7/480)(hcB/kT) \\ &\qquad + (31/8064)(hcB/kT)^2 + (127/92160)(hcB/kT)^3 + \cdots] \qquad (31) \\ &= kT/hcB + 1/3 + (1/15)(hcB/kT) + (4/315)(hcB/kT)^2 \\ &\qquad + (1/315)(hcB/kT)^3 + \cdots \end{aligned}$$

These expressions are never exactly equal to Q, and will in fact always diverge if the series are carried far enough. For small values of hcB/kT, however, the first few terms are an excellent approximation. Thus for $hcB/kT = (1/2)\log 2 = 0.34657$ the first five terms give an error considerably less than 1 in 10^5; the speeds of convergence for the direct and the asymptotic sums are compared in table 1, which gives the fraction contributed to the sum by successive terms. For values of hcB/kT much larger than this, direct summation is the easier process, while for smaller values the asymptotic summation becomes not only increasingly superior to the direct summation but also easier in an absolute sense.

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[2] This result was first derived by Mulholland (80) from the theory of residues, but, in common with all the asymptotic expansions used in this work, it is obtained most easily by using the Euler-Maclaurin expansion formula.

For an actual molecule which differs from the ideal simplicity of a rigid rotator only in the addition of small correction terms due to stretching, as in equation 27, use of the power series expansion[3]

$$\exp.[-(hcD/kT)J^2(J+1)^2 - (hcF/kT)J^3(J+1)^3] = 1 - (hcD/kT)J^2 \times (J+1)^2 - (hcF/kT)J^3(J+1)^3 + (1/2)(hcD/kT)^2J^4(J+1)^4 + \cdots \quad (32)$$

and of asymptotic expansions related to equation 31, which have been published elsewhere (63), leads to

$$\begin{aligned} Q = {} & kT/hcB + 1/3 + (1/315)(hc/kT)(21B - 8D - 6F) + \cdots \\ & - 2(D/B)(kT/hcB)^2 + [12(D/B)^2 - 6(F/B)](kT/hcB)^3 + \cdots \quad (33) \end{aligned}$$

TABLE 1

Comparison of speeds of convergence

Q	Q FIRST FORM	Q SECOND FORM
0.30833	0.97011	0.88960
0.46249	0.02802	0.10277
0.19270	0.00170	0.00712
0.03372	0.00015	0.00047
0.00271	0.00002	0.00004
0.00005		
1.00000	1.00000	1.00000

The first line converges better for high T, the second for low, but for a wide range of temperature, up to beyond 5000°C., both converge with practical rapidity. D is always negative, and in many cases only B and D are known. The empirical energy level formula then leads to absurd results for $J(J + 1) > B/2D$, and the second line of equation 33 eventually diverges. Essentially the same mathematical difficulty is almost always present in a more subtle form. If the empirical energy level formula leads to levels which increase indefinitely with J, the second line of equation 33 will converge; but if there is an upper limit to the levels, as there is for all real molecules, then summation over an infinite number of levels must give an infinite Q. There are actually only a finite number of rotational levels, but this fact does not reduce the pitfalls in a mathematical summation from $J = 0$ to ∞. It can be shown, however, by easy though somewhat

[3] This device was first used by Giauque and Overstreet (30).

inelegant marginal calculations, that whenever the empirical energy-level formula represents the actual levels satisfactorily out to a J such that $(2J + 1)$ exp. $(-\epsilon_J/kT)$ makes a negligible contribution to Q, the successive terms in the second line of equation 33 will decrease, at least until a negligible contribution of similar magnitude is reached. It can be shown further that when the series in equation 33 is broken off at that point, the result is equivalent to breaking off the direct sum at the J value specified above. In practice, this means that the second line of equation 33 can be treated like the first; the successive terms initially decrease, and if they become small enough to be neglected, the series may be broken off without appreciable error; if the terms in either line begin to increase before becoming negligibly small, term-by-term summation is necessary. The second line of equation 33 must always become unsatisfactory for large enough T, but for all molecules for which calculations have as yet been made, the break-down occurs well above the temperature range of interest.

When the molecule is composed of two identical atoms only those states are allowed which have eigenfunctions symmetric for an exchange of nuclei if the nuclei obey the Bose statistics, and only those states which have antisymmetric eigenfunctions if the nuclei obey the Fermi-Dirac statistics. The symmetry of the total eigenfunction depends upon several parts which must be considered separately. All energy levels of diatomic molecules are either positive or negative, according to whether ψ remains constant or changes sign when all positional coordinates (nuclear and electronic) change sign. When $\Lambda > 0$ (Π, Δ $\cdots$ states) each rotational level is a doublet, one member being a positive and the other a negative level. When $\Lambda = 0$ (Σ states) the levels do not have this type of doubling. There are two possibilities here; for Σ^+ states levels with even K are positive and levels with odd K negative, and for Σ^- states levels with even K are negative, levels with odd K positive. For diatomic molecules composed of two chemically identical atoms there is an additional type of symmetry which relates to the electronic eigenfunction alone; when this function is constant on reflection in the origin the state is called even and designated by the subscript g (for German *gerade*); when the function changes sign on reflection the state is odd, designated by u (for *ungerade*). Finally, when the two nuclei are identical, the nuclear spin eigenfunction may be either symmetric or antisymmetric for an exchange of nuclei. Then the total eigenfunction will be symmetric for any of the combinations

even	positive	symmetric spin function
odd	negative	symmetric spin function
even	negative	antisymmetric spin function
odd	positive	antisymmetric spin function

and antisymmetric for the remaining combinations

even	positive	antisymmetric spin function
odd	negative	antisymmetric spin function
even	negative	symmetric spin function
odd	positive	symmetric spin function

Proofs of all these statements have been given in an excellent review by Mulliken (81).

The symmetry properties of the spin eigenfunction are conveniently studied by supposing each spin separately coupled to a strong field. This procedure is permissible, since the number of functions of each type is independent of the coupling scheme. When the spin is zero there is only one atomic spin function, say α, and hence only one molecular spin function, $\alpha(1)\alpha(2)$, which is evidently symmetric. It is very probable that all nuclei with zero spin obey the Bose statistics; when that is so, the allowed combinations are even-positive and odd-negative. Thus, for example, a Σ_u^+ state of a molecule with identical atoms of zero spin must have negative levels and hence can have only odd values of K. For electronic states with $\Lambda > 0$ there are no missing K values, but only one member of each Λ-doublet has the allowed symmetry properties and hence the doubling disappears for homonuclear molecules.

When the nuclear spin is 1/2, its projection on the external field has two eigenvalues, 1/2 and $-1/2$; the corresponding eigenfunctions may be called α and β. It is then possible to construct three symmetric spin functions for the molecule, namely $\alpha(1)\alpha(2)$, $\beta(1)\beta(2)$, and $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$ and one antisymmetric spin function, $2^{-1/2}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$. In general, when the spin is i, there are $2i + 1$ atomic spin functions. Then there are obviously $2i + 1$ symmetric molecular functions of type $\alpha(1)\alpha(2)$ and $(2i + 1)i$ of type $2^{-1/2}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$, a total of $(2i + 1)(i + 1)$. There are $(2i + 1)i$ antisymmetric molecular functions, all of type $2^{-1/2} \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]$.

Under some experimental conditions equilibrium between the states with symmetric and those with antisymmetric spin eigenfunctions is almost completely frozen, and the two states behave as separate chemical species. It is customary to use the term "ortho" for states with symmetric spin functions and "para" for those with antisymmetric spin functions. The normal electron state of H_2 is $^1\Sigma_g^+$; protons obey Fermi-Dirac statistics and have a spin of 1/2; hence for orthohydrogen the spin weight is 3 and only odd J are permitted, while for parahydrogen the spin weight is 1 and even J are required. Deuterons have a spin of 1 and obey Bose statistics; the normal electron state of D_2 is the same as that of H_2; hence orthodeuterium with even J has a spin weight of 6, paradeuterium with odd J a spin weight of 3.

It is evidently necessary to calculate the Q-sum for even J and for odd J separately. It has been shown (63) that for the energy levels of equation 27 and rotational quantum weights $2J + 1$, for unit spin weight

$$\mathbf{Q}(\text{even } J) = \mathbf{Q}(\text{odd } J) = (1/2)\mathbf{Q} \tag{34}$$

Hence for the temperature range to which the asymptotic expansion is applicable, the abundance ratio of ortho and para forms is simply the ratio of their spin weights. For lower temperature, however,

$$\begin{aligned} &Q(\text{odd } J) \to 0 \\ &Q(\text{even } J) \to \text{the spin weight} \end{aligned}$$

and the equilibrium mixture approaches 100 per cent the form with even J. In this temperature range Q for the equilibrium mixture and for the equilibrium frozen at the high temperature value take entirely different courses. The derived thermodynamic functions likewise differ. The discovery of the ortho and para states of hydrogen was an immediate consequence of Dennison's successful calculation of the specific heat of hydrogen on the assumption of a frozen equilibrium; all previous attempts to reproduce the experimental curve by more or less arbitrary quantum weight assignments had been failures. Phenomena of this sort are of the greatest interest both theoretically and experimentally, but of no interest as a problem in calculation. There is nothing to do with the Q-sum except to add it up term by term; since only four or five terms are needed, this is very easy to do.

The calculation which led to equation 33 applies only to $^1\Sigma$ molecules. The calculations become more complicated when $S > 0$, giving multiplet states. A comparatively simple example is the normal state of O_2, a $^3\Sigma_g^-$ with $S = 1$. In Hund case b coupling, which is followed here as in most other Σ states (case a being impossible), the orbital angular momentum Λ and the nuclear angular momentum N combine to give a quantum number K, which has values $\Lambda, \Lambda + 1, \cdots$. In this case $\Lambda = 0$ and $K = 0, 1, 2 \cdots$. K then couples with S to give J. It is the different possibilities in this last coupling which give rise to the multiplicity. Thus for O_2 the three components of the triplet are designated F_1, F_2, F_3 according as $J = K + 1$, K, or $K - 1$. The rotational energy is given by $hc[BK(K + 1) + \cdots] + \tau_i(K)$, where $\tau(K)$ is the K–S coupling energy, which depends upon K and which is slightly different for each member of the multiplet. For $K = 0$ the K–S coupling can give only $J = 1$, and hence only the F_1 component exists. For $K > 0$, all three components are present, the quantum weights being $2J + 1$, hence $2K + 3$, $2K + 1$, $2K - 1$, respectively. For $O^{16}O^{16}$, since the nuclei have zero spin and obey the Bose statistics and since the normal state is $^3\Sigma_g^-$, only odd values of K are allowed.

The most interesting effects due to these multiplet terms are rather sharp maxima in the specific heats at temperatures which may lie below 1°C. or above 100°C., depending upon the separations. When, as in O_2, this electronic heat capacity is excited before the rotational heat capacity approaches its equipartition value, the effect can be studied only by direct summation. For the higher temperatures where asymptotic summation is possible, a comparatively rough treatment of the small multiplet separation is allowable. Thus the separations may be approximated by the empirical equations

$$\left.\begin{aligned}\tau_1(K) - \tau_3(K) &= a(2K+3)^{-1} + b + c(2K+1)\\ \tau_2(K) - \tau_3(K) &= d(2K+1)^{-1} + e + f(2K+1)\end{aligned}\right\} \tag{35}$$

the F_3 state being the lowest. Then

$$\begin{aligned}Q = \sum_{K=1}^{\infty}{}^{(2)} \{&(2K-1) + (2K+1)\,\text{exp.}\,[-(kT)^{-1}\{d(2K+1)^{-1}\\ &+ e + f(2K+1)\}] + (2K+3)\,\text{exp.}\,[-(kT)^{-1}\{a(2K+3)^{-1}\\ &+ b + c(2K+1)\}]\}\, e^{-T(K)/kT}\end{aligned} \tag{36}$$

where

$$T(K) = hc[BJ(J+1) + DJ^2(J+1)^2 + \cdots] \tag{37}$$

is the same for all members of the multiplet and the superscript (2) on Σ indicates summation over alternate values of the index, that is, over odd K. When the exponential terms within the braces are expanded and only the first two terms in each expansion retained, equation 36 becomes

$$\begin{aligned}Q = \sum_{K=1}^{\infty}{}^{(2)} [(3 - 2c)(2K+1) &- (a+d)(kT)^{-1}\\ &- (c+f)(kT)^{-1}(2K+1)]\, e^{-T(K)/kT}\end{aligned} \tag{38}$$

a form very convenient for asymptotic summation.

The normal state of NO is $^2\Pi_{1/2,\,1\,1/2}$, with Hund case a coupling. Here $S = 1/2$ and its projection on the axis, Σ, $= 1/2, -1/2$. Then $\Omega = |\Lambda + \Sigma| = 3/2, 1/2$, measures the total angular momentum parallel to the axis. This combines with the nuclear rotation angular momentum to give J, with allowed values $\Omega, \Omega + 1, \cdots$. Then for $^2\Pi_{1/2}$ the energy is

$$hc\{B_{1/2}[J(J+1) - 1/4] + \cdots\} + \text{const.} \qquad J = 1/2, 3/2 \cdots \tag{39}$$

and for $^2\Pi_{1\,1/2}$

$$hc\{B_{1\,1/2}[J(J+1) - 9/4] + \cdots\} + \text{const.} \qquad J = 3/2, 5/2 \cdots \tag{40}$$

The theoretically interesting terms $-(1/4)hcB_{1/2}$ and $-(9/4)hcB_{1\,1/2}$ in practice frequently are absorbed in the constants, but can of course always be rescued when they are desired. A very pretty method of summation has been suggested by Witmer (107) for case *a* molecules. The rotational and vibrational constants for all members of the multiplet are assumed equal as a first approximation. Then the summation over J for a single member gives

$$\mathbf{Q}_{\text{rot}} = kT/hcB + 1/3 + (hcB/kT)(1/15 - \Omega_s^2/6) \tag{41}$$

for J integral, as is shown by the argument in the following section where l plays exactly the same mathematical rôle as Ω_s and gives a similar expression with only a feeble dependence on Ω_s for the other possible cases (half-integral J, alternate J values). The multiplet spacing in case *a* is uniform, the positions being given by a term $(s-1)\Delta$. Then as a first approximation the multiplet structure contributes a factor to $\mathbf{Q}$

$$\begin{aligned} Q_{\text{mult}} &= 1 + e^{-hc\Delta/kT} + e^{-2hc\Delta/kT} + \cdots + e^{-(m-1)hc\Delta/kT} \\ &= (1 - e^{-mhc\Delta/kT})/(1 - e^{-hc\Delta/kT}) \end{aligned} \tag{42}$$

This factor is the ratio of two vibrational factors, and the contribution to the thermodynamic functions is thus the difference between two vibrational contributions. The contribution to $\mathbf{C}$ passes through a maximum the height of which depends only on m, approaching R as m increases. The contribution to $\mathbf{H}$ reaches a limiting value of $(1/2)(m-1)\Delta$ and that to $\mathbf{S}$ and $-\mathbf{F}/T$ a limiting value of $R \log m$ as T increases.

If the rotational and vibrational constants are too greatly different for the various members of the multiplet, the anharmonic term associated with Witmer's calculation would be inconveniently large, and separate treatment of each member would be easier. In any case, formulas for sums over half integral J values are needed. These have been given elsewhere (63).

The rotational sum for polyatomic molecules

The simplest polyatomic molecules are linear, but even these lead to complexities absent in the diatomic case. The linear triatomic molecule has been shown by Dennison (17) to have two stretching vibrations, ω_1 and ω_3, and a double bending vibration ω_2 with a subsidiary azimuthal quantum number l which measures the angular momentum of the bending vibrations parallel to the molecular axis. The allowed values of l are $-v_2, -v_2+2, \cdots v_2-2, v_2$, where v_2 is the quantum number for the vibration ω_2. The allowed values of J are $J \geqq |l|$. The first approximation to the rotational energy is

$$E = hcB[J(J+1) - l^2] \tag{43}$$

Then if the molecule is unsymmetrical, so that there are no alternating weights for the rotational levels due to spin and symmetry,

$$\begin{aligned}\mathbf{Q} &= e^{(hcB/kT)(l^2+1/4)}\,[kT/hcB + 1/12 + (7/480)(hcB/kT) + \cdots]\\ &\quad - e^{(hcB/kT)l^2} - 3e^{(hcB/kT)(l^2-2)} - \cdots - (2l-1)\,e^{(hcB/kT)(l^2-l^2-l)}\\ &= e^{(hcB/kT)(l^2+1/4)}[kT/hcB + 1/12 + (7/480)(hcB/kT) + \cdots]\\ &\quad - l^2 - (1/2)(hcB/kT)(l^4+l^2) - \cdots = kT/hcB + 1/3\\ &\quad + (hcB/kT)(1/15 - l^2/6) + \cdots\end{aligned} \tag{44}$$

This result is in a form suitable for use in summing over l, a step which is part of the vibrational treatment. The method used here can be applied equally well when the desired sum extends over only alternate J values.

The rotations of non-linear polyatomic molecules are vastly more complicated. The quantum mechanical treatment of a rigid symmetrical top with moments of inertia A, A, C gives the energy levels

$$E = (h^2/8\pi^2A)[K(K+1) + n^2(A/C-1)] \qquad |n| \leqq K \tag{45}$$

with a quantum weight of $2K + 1$ for each pair K, n. (If only positive n are considered, the quantum weight is $2(2K + 1)$ for $n > 0$). Then

$$Q = \sum_{K=0}^{\infty}\ \sum_{n=-K}^{K} \exp. - (h^2/8\pi^2AkT)[K(K+1) + n^2(A/C-1)] \tag{46}$$

The asymptotic expansion of this double sum has been shown (103, 63, 104) to be

$$\begin{aligned}\mathbf{Q} = \pi^{1/2}\sigma^{-3/2}e^{\sigma/4}(\beta+1)^{-1/2}[1 &+ (1/12)\beta(\beta+1)^{-1}\sigma\\ &+ (7/480)\beta^2(\beta+1)^{-2}\sigma^2 + \cdots]\end{aligned} \tag{47}$$

where

$$\begin{aligned}\sigma &= h^2/8\pi^2AkT\\ \beta &= A/C - 1\end{aligned} \tag{48}$$

Asymptotic formulas have also been given (63) by which stretching effects expressed as higher powers of $K(K + 1)$ and n^2, as well as cross products, can be treated. The asymmetrical top has been solved quantum mechanically, but it is hard to make much use of the results owing to their complicated form. There are still the same quantum numbers K, n and the same weights as before, but there is no closed formula for the energy levels. Instead, when K is even the levels are given as the roots of three algebraic equations of degree $K/2$ and one of degree $K/2 + 1$; when K is odd they are the roots of three equations of degree $(K + 1)/2$ and one of degree

$(K - 1)/2$. The expansion for the symmetrical case, however, may be written

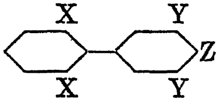
$$\mathbf{Q} = \pi^{1/2}(h^2/8\pi^2kT)^{3/2}(A^2C)^{-1/2} + \cdots \tag{49}$$

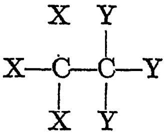
and one might guess that for the asymmetrical top

$$\mathbf{Q} = \pi^{1/2}(h^2/8\pi^2kT)^{3/2}(ABC)^{-1/2} + \cdots \tag{50}$$

Gordon (36) has shown by numerical calculations that this is correct.

Many polyatomic molecules possess internal rotations as well as external. It will be understood readily that little progress has been made in the theoretical treatment of rotation in such cases and *a fortiori* in the calculation of the **Q**-sum. The model of ethane—two identical coaxial symmetrical tops—has been solved both for free rotation (78) and for an assumed potential function (83). The model of tetramethylmethane has been solved for the case of free rotation (68). Asymptotic expansions have been found for **Q** in both cases of free rotation (78, 65). Eidinoff and Aston (19) have obtained the first term in **Q**, corresponding to replacing the summations by integrals, for the more general case of two coaxial asymmetric tops, the common axis being a principal axis for each. Typical molecules are[4]





$$\begin{matrix} & & X & & Y & & \\ & & & & \mid & & \\ X & - & C & - & C & - & Y \\ & & \mid & & \mid & & \\ & & X & & Y & & \end{matrix}$$

where X, Y, Z are atoms or linear radicals, such as $-C{\equiv}N$. The general method used by Eidinoff and Aston has been further developed by Kassel (66a), and applied to a number of more complex cases, including propane, butane, isobutane, propylene, 1-butene, *cis*- and *trans*-2-butenes, isobutene, trimethylethylene, tetramethylethylene, butadiene, and all the methyl derivatives of benzene. The assumption of perfectly free rotation cannot be entirely correct in any of these cases; even if there were no real potential energy resisting rotation, there would still be the pseudo-potential energy discovered by Kassel (66), caused by change of vibration frequencies with change of angle. In the case of butane, this pseudo-potential energy amounts to about 50 cal. For most of the molecules listed above the

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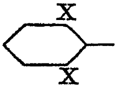
[4] The symmetrically substituted groups such as  have three different moments of inertia, hence are asymmetrical tops; if substitution were unsymmetrical, the tops would not be coaxial. The group CX_3, however, is a symmetrical top.

true potential energy also is likely to be small, and the assumption of free rotation should give fair results. When there are dipole moments, as in ethylene chloride, or large rotating groups, as in triphenylmethane, or long floppy chains whose ends could strike, as in hexane, the assumption of free rotation would not be permissible. In such cases there is no way known by which thermodynamic calculations could be made.

The application of symmetry considerations to polyatomic molecules presents very considerable difficulties. Hund (48) solved the problem for ammonia, and Elert (20) applied his method to methane; but greatly simplified calculations for these molecules, as well as for benzene, trimethylene, ethylene, and several others, have been made by Wilson (106) with the aid of group theory methods. As an example of the procedure which must be used to obtain the Q-sum in such cases, a brief treatment of CH_4 and CD_4 is given here; this calculation has not been published elsewhere.

For the methane framework there are three symmetry types, *A*, *E*, and *T*, which play a rôle similar to the two types *S* and *A* (not the same *A*) for diatomic molecules. When the product of electronic and vibrational eigenfunctions has the symmetry *A*, as is the case for the non-vibrating normal state, the weights for each symmetry type of nuclear spin eigenfunction are as follows:

ψ_{spin}	$J = 6p$	$J = 6p + 1$	$J = 6p + 2$	$J = 6p + 3$	$J = 6p + 4$	$J = 6p + 5$
A.............	$5p + 5$	$5p$	$5p$	$5p + 5$	$5p + 5$	$5p$
E.............	$2p$	$2p$	$2p + 2$	$2p$	$2p + 2$	$2p + 2$
T.............	$9p$	$9p + 3$	$9p + 3$	$9p + 6$	$9p + 6$	$9p + 9$
Total........	$16p + 5$	$16p + 3$	$16p + 5$	$16p + 11$	$16p + 13$	$16p + 11$

All the weights in this table must be multiplied by $2J + 1$ to obtain the total quantum weight for a given J and spin symmetry; it should perhaps be mentioned explicitly that since methane is a top with three equal moments the quantum number n effectively disappears. Any weight factors which can be represented by a table of this sort can be expressed analytically by a weight factor

$$G(2ap + 2b + 1)\,[(2ap + 2b + 1) + f(b)]$$

for the level $J = ap + b$, where the constant G depends upon the symmetry type of the nuclear spin function. Then

$$\begin{aligned} Q &= \sum_{b=0}^{a-1} \sum_{p=0}^{\infty} G(2ap + 2b + 1)[(2ap + 2b + 1) + f(b)]\, e^{-J(J+1)\sigma} \\ &= \sum_{J=0}^{\infty} G(2J + 1)^2 e^{-J(J+1)\sigma} + \sum_{b=0}^{a-1} \sum_{p=0}^{\infty} Gf(b)\,(2ap + 2b + 1) e^{-J(J+1)\sigma} \end{aligned} \tag{51}$$

$$\mathbf{Q} = G\pi^{1/2}e^{\sigma/4}\sigma^{-3/2} + G\sum_{b=0}^{a-1} f(b)X(b) \tag{52}$$

where

$$\begin{aligned} X(b) = e^{-b(b+1)\sigma}\{1/a\sigma + b + 1/2 - a/6 \\ + \sigma\,[(a/12)(2b+1)^2 - a^3/60] + \cdots\} \end{aligned} \tag{53}$$

The first asymptotic expansion has already been given and the second is easily made. Now by the substitution $b = a - 1 - b_0$ in $X(b)$ and expansion of part of the exponential it can be shown that

$$X(a - 1 - b) = X(b) \tag{54}$$

In Wilson's weight tables, partly reproduced above,

$$f(a - 1 - b) = -f(b) \tag{55}$$

for all nuclear spin symmetry types for all electronic-vibrational symmetry types for both CH_4 and CD_4. Hence in all these cases

$$\sum_{b=0}^{a-1} f(b)X(b) = 0 \tag{56}$$

and

$$\mathbf{Q} = G\pi^{1/2}e^{\sigma/4}\sigma^{-3/2} \tag{57}$$

For the particular case being considered, the normal state of methane, $G = 5/12$, $1/6$, and $3/4$ for A, E, T spin symmetries respectively, or $4/3$ for the three together. This same factor $4/3$ is given by the empirical rule that the effective weight is the product of the spin multiplicities for all the atoms divided by the symmetry number of the molecule, here $2^4/12 = 4/3$. For the corresponding states of CD_4 the weights are $5/4$, 1, $9/2$, a total of $27/4 = 3^4/12$. The range of validity of these asymptotic expansions has been tested by direct summation. For $\sigma = 0.11512925$, for CH_4

$$Q = 62.27472 \qquad \mathbf{Q} = 62.26373 \qquad Q/\mathbf{Q} = 1.00018$$

and for CD_4

$$Q = 315.23487 \qquad \mathbf{Q} = 315.21013 \qquad Q/\mathbf{Q} = 1.000078$$

For $\sigma = 0.23025851$, for CH_4

$$Q = 23.12567 \qquad \mathbf{Q} = 22.65636 \qquad Q/\mathbf{Q} = 1.0207$$

The asymptotic expansion thus fails for σ only a little greater than 0.1, very considerably sooner than is the case with the simple symmetrical top, where for $\sigma = 0.2302585092994046$

$$Q = 16.99227012072823 \qquad \mathbf{Q} = 16.99227012072823$$

For CH_4, $\sigma = 0.1$ is at 72°K., $\sigma = 0.23$ at 31.5°K. There is thus little likelihood that any calculations ever will be needed for which Q is not satisfactory for this or any other polyatomic molecule; should such calculations prove necessary, however, they could always be made by direct summation with comparative ease.

The vibrational sum

The next operation to be considered is the summation over vibrational states. Since it is an experimental fact that B_v, D_v, etc. can be represented by rapidly converging power series in v, the result of the rotational summation may be put in the form

$$\mathbf{Q}(v) = K_0 + K_1 v + K_2 v^2 + \cdots \tag{58}$$

for a diatomic molecule, or a similar power series expansion in several variables for a polyatomic molecule. Then

$$\begin{aligned}\mathbf{Q} &= \sum_{v=0}^{\infty} \mathbf{Q}(v) \exp.[-hc(\omega_0 v - x\omega_0 v^2 + \cdots)/kT] \\ &= \sum_{v=0}^{\infty} P(v) \exp.[-hc\omega_0 v/kT]\end{aligned} \tag{59}$$

where $P(v)$ is the product of $\mathbf{Q}(v)$ and the power series expansion of exp. $[-hc(-x\omega_0 v^2 + \cdots)/kT]$. An exact term-by-term evaluation of this sum is possible by means of the following formulas (61), where

$$z = e^{-hc\omega_0/kT} \tag{60}$$

$$(1 - z)^{-1} f_i = \sum_{v=0}^{\infty} v^i z^v \tag{61}$$

$$\begin{aligned}
f_0 &= 1 \\
f_1 &= z(1 - z)^{-1} \\
f_2 &= z(1 + z)(1 - z)^{-2} \\
f_3 &= z(1 + 4z + z^2)(1 - z)^{-3} \\
f_4 &= z(1 + 11z + 11z^2 + z^3)(1 - z)^{-4} \\
f_5 &= z(1 + 26z + 66z^2 + 26z^3 + z^4)(1 - z)^{-5} \\
f_6 &= z(1 + 57z + 302z^2 + 302z^3 + 57z^4 + z^5)(1 - z)^{-6} \\
f_7 &= z(1 + 120z + 1191z^2 + 2416z^3 + 1191z^4 + 120z^5 + z^6)(1 - z)^{-7} \\
f_8 &= z(1 + 247z + 4293z^2 + 15619z^3 + 15619z^4 + 4293z^5 + 247z^6 + z^7) \\
&\quad \times (1 - z)^{-8}
\end{aligned} \tag{62}$$

The result of the vibrational summation with the use of these formulas is then (for a diatomic molecule)

$$\mathbf{Q} = (\mu kT/hcB_0)(1 - z)^{-1} \sum_{i=0}^{\infty} f_i g_i \tag{63}$$

Here the first factor contains the contribution from a rigid rotator with moment of inertia $h/8\pi^2cB_0$, the constant μ taking care of symmetry and of nuclear spin, the second factor the contribution of a harmonic oscillator of frequency $c\omega_0$, and the third factor all corrections for stretching, anharmonicity, missing levels, etc. In this factor the f_i are the previously given functions and the g_i are power series in T and $1/T$ with numerical coefficients (Laurent series). It is clear from the form of the fundamental equations that each factor in $\mathbf{Q}$ makes an additive contribution to the thermodynamic functions. The rotational factor gives (per mole)

$$\begin{aligned} \mathbf{H}_{\text{rot}} &= RT \qquad \mathbf{C}_{\text{rot}} = R \\ \mathbf{S}_{\text{rot}} &= R + R \log \mu k/hcB_0 + R \log T \\ -\mathbf{F}_{\text{rot}}/T &= R \log \mu k/hcB_0 + R \log T \end{aligned} \tag{64}$$

The vibrational factor gives

$$\begin{aligned} \mathbf{H}_{\text{vib}} &= R(hc\omega/k)[z/(1-z)] \\ \mathbf{C}_{\text{vib}} &= R(hc\omega/kT)^2[z/(1-z)^2] \\ \mathbf{S}_{\text{vib}} &= R(hc\omega/kT)[z/(1-z)] - R \log (1-z) \\ -\mathbf{F}_{\text{vib}}/T &= -R \log (1-z) \end{aligned} \tag{65}$$

Several convenient tables of these vibrational contributions, often called Einstein functions, are available (69, 82).

The anharmonic factor is

$$h = \sum_i f_i g_i \tag{66}$$

Then

$$h' = \sum_i (f_i g_i' + f_i' g_i) \tag{67}$$

$$h'' = \sum_i (f_i g_i'' + 2f_i' g_i' + f_i'' g_i) \tag{68}$$

where, as always in this paper, a $'$ means differentiation with respect to $1/T$. The g_i can be differentiated at sight. The derivatives of the f_i, which have not been published previously, are

$$\begin{aligned} f_0' &= 0 \\ f_1' &= -(hc\omega/k)z(1-z)^{-2} \\ f_2' &= -(hc\omega/k)z(1+3z)(1-z)^{-3} \\ f_3' &= -(hc\omega/k)z(1+10z+7z^2)(1-z)^{-4} \\ f_4' &= -(hc\omega/k)z(1+25z+55z^2+15z^3)(1-z)^{-5} \\ f_5' &= -(hc\omega/k)z(1+56z+276z^2+236z^3+31z^4)(1-z)^{-6} \\ f_6' &= -(hc\omega/k)z(1+119z+1134z^2+2114z^3+889z^4 \\ &\qquad +63z^5)(1-z)^{-7} \end{aligned} \tag{69}$$

$$
\begin{aligned}
f_7' &= -(hc\omega/k)z(1 + 246z + 4173z^2 + 14428z^3 + 13203z^4 \\
&\qquad + 3102z^5 + 127z^6)(1-z)^{-8} \\
f_8' &= -(hc\omega/k)z(1 + 501z + 14361z^2 + 83941z^3 + 140571z^4 \\
&\qquad + 72615z^5 + 10315z^6 + 255z^7)(1-z)^{-9} \\
f_0'' &= 0 \\
f_1'' &= (hc\omega/k)^2 z(1+z)(1-z)^{-3} \\
f_2'' &= (hc\omega/k)^2 z(1 + 8z + 3z^2)(1-z)^{-4} \\
f_3'' &= (hc\omega/k)^2 z(1 + 23z + 41z^2 + 7z^3)(1-z)^{-5} \\
f_4'' &= (hc\omega/k)^2 z(1 + 54z + 240z^2 + 170z^3 + 15z^4)(1-z)^{-6} \\
f_5'' &= (hc\omega/k)^2 z(1 + 117z + 1052z^2 + 1772z^3 + 627z^4 \\
&\qquad + 31z^5)(1-z)^{-7} \\
f_6'' &= (hc\omega/k)^2 z(1 + 244z + 3997z^2 + 12992z^3 + 10787z^4 \\
&\qquad + 2156z^5 + 63z^6)(1-z)^{-8} \\
f_7'' &= (hc\omega/k)^2 z(1 + 499z + 13995z^2 + 78577z^3 + 123727z^4 \\
&\qquad + 58221z^5 + 7093z^6 + 127z^7)(1-z)^{-9} \\
f_8'' &= (hc\omega/k)^2 z(1 + 1010z + 46590z^2 + 421930z^3 + 1122560z^4 \\
&\qquad + 997974z^5 + 290050z^6 + 22670z^7 + 255z^8)(1-z)^{-10}
\end{aligned}
\qquad (70)
$$

It is convenient to calculate the anharmonic correction at a few widely spaced temperatures, say 250, 500, 750, 1000, 2000, 3000, 4000, and 5000°K., and fit the results by least squares to

$$
\mathbf{F}_{\text{anh}}/T = a + b/T + c \log T + dT + eT^2 \qquad (71)
$$

and the thermodynamically consistent equations for $\mathbf{H}_{\text{anh}}$ and $\mathbf{C}_{\text{anh}}$. Values at intermediate temperatures are given by the resulting equations with an error considerably less than 0.001 cal. per degree when the underlying calculations are made with equal accuracy.

In the case of polyatomic molecules with no two vibrations of the same frequency the procedure is obvious. When there are n identical frequencies the level $vhc\omega$ has a quantum weight $(n + v - 1)!/(n - 1)!v!$, which is a polynomial in v and could be multiplied out into $P(v)$. It is much more convenient to proceed a little differently, however, as indicated by the following example with $n = 4$. The weight factor is then $(1/6)(v + 1)(v + 2)(v + 3)$. Define

$$
(1 - z)^{-4} m_i = \sum_{v=0}^{\infty} (1/6)(v + 1)(v + 2)(v + 3)\, v^i z^v \qquad (72)
$$

so that m_i will play a rôle analogous to the previously used f_i. Then it is easily shown by using the formulas for f_i that

$$
\begin{aligned}
m_0 &= 1 \\
m_1 &= 4z(1 - z)^{-1} \\
m^2 &= 4z(1 + 4z)(1 - z)^{-2} \\
m^3 &= 4z(1 + 13z + 16z^2)(1 - z)^{-3} \\
m^4 &= 4z(1 + 32z + 113z^2 + 64z^3)(1 - z)^{-4}
\end{aligned}
\qquad (73)
$$

Tables of the derivatives m'_i and m''_i can then be prepared and used in exactly the same way as f'_i and f''_i. This procedure has the very great advantage of isolating the complete harmonic factor $(1 - z)^{-4}$ and keeping a relatively small anharmonic contribution.

It is to be expected that the higher levels will be somewhat less degenerate than simple theory indicates. An example is furnished by the linear triatomic molecule which has been shown by Dennison (17) to have two single valence vibrations ω_1 and ω_3 and one double bending vibration ω_2. The energy is

$$\begin{aligned} E = hc[\omega_1 v_1 + \omega_2 v_2 + \omega_3 v_3 - a v_1^2 - b\{v_2^2 - (1/3)l^2\} - c v_2^2 - d v_1 v_2 \\ - e v_1 v_3 - f v_2 v_3 + \text{higher terms}] \qquad (74) \end{aligned}$$

where l is a subsidiary azimuthal quantum number with values $-v, -v + 2, \cdots v - 2, v$. Then the degeneracy is removed when l is considered, and

$$Q = \sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \sum_{v_3=0}^{\infty} \sum_{l=-v_2}^{+v_2}{}^{(2)} e^{-E/kT} \qquad (75)$$

where $\Sigma^{(2)}$ means summation over alternate values of the index. In handling this summation the first of the following formulas is necessary; if higher anharmonic terms are to be considered, the second one also will be needed.

$$\begin{aligned} \sum_{-v}^{+v}{}^{(2)} l^2 &= (v/3)(v + 1)(v + 2) \\ \sum_{-v}^{+v}{}^{(2)} l^4 &= (v/15)(v + 1)(v + 2)(3v^2 + 6v - 4) \end{aligned} \qquad (76)$$

The resulting formula for Q has been published elsewhere (64) and need not be repeated here. It consists of harmonic and anharmonic factors and hence is convenient for computation. Similar methods undoubtedly can be used for more complex polyatomic molecules whenever the spectroscopic data become available.

Another complication which can arise in polyatomic molecules is degeneracy involving unequal frequencies whose ratio is approximately that of two small integers. Thus in carbon dioxide ω_1 is almost exactly $2\omega_2$, and there are as a result perturbations of the order of 50 cm.$^{-1}$ in the positions of the levels from locations based on a simple equation such as equation 74. An exact analysis of the data for carbon dioxide has been given by Adel and Dennison (1), and their equations have made possible exact calculation of **Q** (64). The computations are somewhat lengthy, however, and since rather special methods are needed the details will not be discussed here.

An alternative method of vibrational summation

An alternative method has been developed by Gordon and Barnes (42) and extended by Gordon (38). Consider an unsymmetrical $^1\Sigma$ diatomic molecule with energy levels given by

$$E = hc[(v + 1/2)\omega_e - (v + 1/2)^2\omega_e x + B_v(J + 1/2)^2 + D_v(J + 1/2)^4 + F_v(J + 1/2)^6] \tag{77}$$

Put

$$q_v = kT/B_v hc \qquad d_v = -2(D_v/B_v)q_v \qquad f_v = -6(F_v/B_v)q_v^2 \tag{78}$$

In this notation equation 33 becomes

$$\mathrm{Q}_{\mathrm{rot}} = e^{1/4q_v} q_v(1 + 1/12q_v + d_v + 3d_v^2 + f_v + \ldots) \tag{79}$$

Now use the unconventional representation

$$B_v = B_0/(1 + \beta_1 v + \beta_2 v^2) \tag{80}$$

Then

$$\mathrm{Q}_{\mathrm{rot}} = e^{1/4q_0} q_0(1 + \beta_1 v + \beta_2 v^2)(1 + 1/12q_0 + d_0 + 3d_0^2 + f_0) + \text{higher terms} \tag{81}$$

and

$$\mathrm{Q} = Q_V e^{1/4q_0} q_0(1 + \beta_1\bar{v} + \beta_2\bar{v}^2)(1 + 1/12q_0 + d_0 + 3d_0^2 + f_0) \tag{82}$$

where

$$\begin{aligned} Q_V &= \sum_v e^{-\epsilon_v hc/kT} \\ \bar{v} &= (1/Q_V) \sum_v v e^{-\epsilon_v hc/kT} \\ \overline{v^2} &= (1/Q_V) \sum_v v^2 e^{-\epsilon_v hc/kT} \end{aligned} \tag{83}$$

It is at this point that Gordon and Barnes introduce the essential feature of their method. It is evident that log Q_V, $\bar{v}$, and $\bar{v}^2$ are functions of $hc\omega_e/kT$ and x. They give double-entry tables for these three functions as well as for a number of others needed in calculating Q' and Q''. Once these tables have been prepared the thermodynamic functions can be computed somewhat more rapidly than in the purely analytic way. The method is somewhat inflexible, but not to the extent that might be imagined. It lacks the capability of making calculations of unlimited precision, but it has been shown to yield accuracy as great as is aimed at in most current calculations. The account of the method given here is very incomplete; it must not be thought that the space devoted to it is a measure of the utility of the technique.

IV. APPLICATIONS

Methods

Thermodynamic functions obtained by the methods of the foregoing pages may of course be used in exactly the same ways that have now become classical for functions obtained from experimental specific heats, equilibrium constants, electromotive force values, etc. Somewhat different procedures, however, may be used with advantage. Both H and F as given by these calculations are referred to the gas at 0°K., that is, in the non-vibrating, non-rotating, non-translating state of lowest electronic energy. This is frequently indicated by writing $F^0 - E_0^0$ in place of F. It is necessary to correct the purely spectroscopic "ΔF" for a reaction by adding ΔE_0^0. When accurate spectroscopic dissociation energies are known, ΔE_0^0 can be obtained directly; then to calculate equilibrium constants it is necessary to calculate spectroscopic values only for F/T, and hence only Q is needed. When a calorimetric heat of reaction is used, it is necessary to calculate H up to the temperature of the calorimetry to obtain ΔE_0^0, but equilibrium constants for higher temperatures may then be obtained from F/T. Even when all the thermodynamic functions have been computed, the foregoing method is considerably more expeditious than the more conventional procedures that have sometimes been used. Likewise it will be found that H is far more useful than C_p, and the habit of talking about specific heat when only integrated values are actually used should not mislead one into graphical integrations of spectroscopic C_p values.

Historical

The earliest actual calculations seem to be those of Urey (97), Tolman and Badger (95), and Hicks and Mitchell (47), all dealing with HCl. In all these calculations incorrect quantum weights were used. Giauque and Wiebe (31) made the first correct calculation of the entropy of HCl, and Hutchisson (49) the first correct calculation of its specific heat. Meanwhile Dennison (16), assuming a frozen ortho–para equilibrium, had successfully calculated the specific heat of hydrogen. The method was thus well-established in 1928, though the development of convenient mathematical techniques came somewhat later.

Results of calculations

In the following pages there is an attempt to include all but the most trivial calculations that have been made. Compounds are arranged according to the system used in the International Critical Tables; the key-numbers used here are

O	H	Cl	Br	I	S	N	C
1	2	4	5	6	8	11	16

All isotopes of an element are assigned the same key number. Equilibria are discussed under the component of highest key number.

Atomic oxygen, O. Values of $-F/T$ for atomic oxygen have been tabulated by Johnston and Walker (58); a few minor corrections to these values were published later (59).

Molecular oxygen, O_2. Johnston and Walker (57) calculated C_p, S, and $-F/T$ to 5000°K., taking account of the normal ${}^3\Sigma_g^-$ state and the ${}^1\Sigma_g^+$ state at 1.62 v. above the normal. They omitted the ${}^1\Delta$ level, which had been predicted to lie 0.8 v. above the normal state but had not yet been observed. They (58) combined their $-F/T$ values with a spectroscopic heat of dissociation to calculate equilibrium constants for

$$O_2 = 2O$$

Spencer and Justice (93) gave an empirical equation to fit the spectroscopic C_p values. Lewis and von Elbe (71) calculated from the excess observed specific heat of O_2 in O_3 explosions over Johnston and Walker's values that the ${}^1\Delta$ state lay 0.75 v. above the normal; revision (74) of this calculation, with correction for temperature gradients in the bomb, subsequently gave 0.85 v. Meanwhile Herzberg (46) had observed the 0, 0 band of the system ${}^3\Sigma_g^-$–${}^1\Delta_g^+$ at 7881.6 cm.$^{-1}$, thus definitely fixing the ${}^1\Delta$ state 0.97 v. above the normal, and Johnston and Walker (60) had recalculated their earlier values of C_p, S, and $-F/T$ for O_2 and of K for the dissociation

$$O_2 = 2O$$

from 1000 to 5000°K. and given a complete table for H from 90.13° to 5000°K. The agreement between the position of the ${}^1\Delta$ level, as determined by spectroscopy and as estimated by Lewis and von Elbe from experimental specific heats in combination with the incomplete spectroscopic values, is really excellent. This will be realized when it is stated that at 2500°K., slightly above the highest explosion temperatures, a ${}^1\Delta$ level at 0.97 v. increases H by 160 cal., and one at 0.85 v. by 250 cal. This difference of 90 cal. amounts to a temperature difference of less than 10°C., and is in the direction to be accounted for by a slight heat loss during the explosion.

Molecular oxygen, O_2^{18}. Urey and Greiff (98) calculated the ratio of Q (including the translational part) for O_2^{18} to that for O_2^{16} at 273.1, 293.1, and 600°K.; these values are referred to the non-vibrating state as a zero of energy and are thus immediately applicable to the calculation of equilibrium constants in isotopic exchange reactions. In what follows this somewhat specialized Q will be designated f, following the notation used by Urey and Greiff.

Ozone, O_3. Kassel (62) calculated approximate values of $-F/T$ for ozone up to 5000°K. on the basis of an approximate frequency assignment, and from the thermochemical heat of formation of ozone calculated K for

$$O_3 = O_2 + O$$

and

$$O_3 = \tfrac{3}{2}O_2$$

The results showed that earlier experimental attempts to determine the entropy of ozone by electromotive force measurements and also by the formation of ozone when filaments were heated in liquid oxygen (24) had given wholly incorrect values. The maximum concentration of ozone in the system O–O_2–O_3 at equilibrium at a total pressure of 1 atm. is 10^{-6} atm. at 3500°K.; at all temperatures above 900°K. O is more abundant than O_3. The 1 per cent of ozone formed in liquid oxygen must have been due to the escape of atomic oxygen from the hot region; the mole fraction of O at 2300°K. is about 0.5 per cent, a value of the right order of magnitude to support this interpretation. The same spectroscopic data were used later to calculate H for ozone up to 1000°K.; the values may be found in the useful tabulation of Lewis and von Elbe (73).

Atomic hydrogen, H. Giauque (25) has tabulated $-F/T$ to 5000°K.

Deuterium, D. Johnston and Long (55, 56) have tabulated $-F/T$ to 3000°K.

Molecular hydrogen, H_2. The first successful spectroscopic calculations for hydrogen were the historic specific-heat calculations of Dennison (16), in which a rigid molecule was assumed, and hence no high accuracy was obtained. Giauque (25) used the actual energy levels to calculate the equilibrium ortho–para ratio up to 298.1°K., where the composition is 25.074 per cent para, S at 298.1°K., H and C_p up to 298.1°K. for pure ortho, pure para, the 3:1 mixture, and the true equilibrium composition, and $-F/T$ from 298.1°K. to 5000°K. Using the spectroscopic heat of dissociation given by Richardson and Davidson (85), he calculated also the equilibrium constant for

$$H_2 = 2H$$

obtaining values surprisingly close to the experimental results of Langmuir (70). The calculated entropy agreed with the experimental third law value only when the entropy of mixing of ortho and para states in the solid, $-(R/4)\log 1/4 - (3R/4)\log 1/12$, was added to the observed value. The controversy concerning the legitimacy of this addition has now subsided and need not be revived here. Gordon and Barnes (40) calculated approximate values for C_p and S up to 1200°K. Davis and Johnston (15) subsequently calculated C_p, H and S to 5000°K.; they also gave a corrected table for $-F/T$ which replaces the corresponding values given by Giauque, and gave a few additional corrections to Giauque's calculations. Empirical equations for C_p have been given by Spencer and Justice (93) and by Chipman and Fontana (8), both based on Davis and Johnston's calculations.

HD *and* D_2. Urey and Rittenberg (99) used theoretical spectroscopic relations to calculate the rotation-vibration levels of HD and of D_2 from those of H_2, and used these levels to calculate $-F/T$ from 50 to 700°K. and also the equilibrium constant for

$$H_2 + D_2 = 2HD$$

Johnston and Long (55) calculated C_p, H, S, and $-F/T$ for HD and D_2 up to 3000°K. They give C_p and H for D_2 for the pure para form, the pure ortho form, the 1:2 ratio, and the true equilibrium composition at temperatures up to 300°K.; at higher temperatures the values become essentially identical for all four cases. The calculated ortho–para equilibrium ratios have been confirmed by Farkas, Farkas, and Harteck (23). Farkas and Farkas (22) showed that the equilibrium constant for

$$H_2 + D_2 = 2HD$$

was about 4. More precise measurements by Rittenberg, Bleakney, and Urey (86) checked closely with the theoretical values over the range 298 to 741°K. Later experiments by Gould, Bleakney, and Taylor (44) using Cr_2O_3 and Ni catalysts to obtain equilibrium carried this confirmation down to 83°K., where $K = 2.2$.

OH. Villars (100, 101) calculated S_{298}, but made an error in electronic quantum weights. The lowest states of OH are an inverted $^2\Pi_{1/2,\,1\,1/2}$ doublet, each level of which has of course Λ-type doubling, which in this case is unusually large (due to the small moment of momentum). Johnston and Dawson (53) calculated C_p from 0.01 to 5000°K., the lower part of this range being of course only an amusing exercise. The Λ-doubling contribution to C_p reaches a maximum at 0.060°K., the $^2\Pi_{1/2}$ excitation contribution a maximum at 100°K., which is about the point where the rotation has become fully developed. Johnston and Dawson also calculated S from 250 to 5000°K. and H and $-F/T$ from 298.1° to 5000°K. The underlying spectroscopic data are precise, but exact equilibrium constants cannot be calculated since no heat of reaction involving OH is precisely known. Lewis and von Elbe (72), however, have determined an approximate value for ΔH_0 for

$$H_2O = OH + \frac{1}{2}O_2$$

This reaction is discussed in the following paragraph.

Water, H_2O. Gordon and Barnes (40) calculated rough values for C_p and S from 400° to 1200°K. Gordon (35) used somewhat more accurate data to calculate $-F/T$ to 3000°K. Finally, taking into account anharmonic terms and rotation-vibration interactions, Gordon (36) gave precise values for $-F/T$, S, and C_p to 1500°K. and less accurate values (37) up to 3000°K. Spencer and Justice (93) gave an empirical equation to represent these C_p values.

Lewis and von Elbe (73) used the data of Giauque (35) on H_2, of Johnston and Walker (57) on O_2 with an approximate correction for the $^1\Delta$ level, and Gordon's final values for H_2O, together with $\Delta H_0 = -57,111$ cal., based on Rossini's (90) precise heat of combustion of hydrogen, to calculate equilibrium constants for

$$H_2 + \frac{1}{2}O_2 = H_2O$$

from 300° to 3000°K. They used the same data for H_2 and H_2O, together with their (72) explosion value of $\Delta H_0 = -63{,}000$ cal. to calculate equilibrium constants for

$$OH + \frac{1}{2}H_2 = H_2O$$

from 300° to 3000°K.

Water, H_2O^{18}. Urey and Greiff (98) calculated the ratio of f values for H_2O^{18} and H_2O^{16} at 273, 298, and 600°K., and the equilibrium constant for

$$O_2^{16} + 2H_2O^{18}(g) = O_2^{18} + 2H_2O^{16}(g)$$

at the same temperatures, the values being 1.048, 1.041, and 1.006.

HDO *and* D_2O. Topley and Eyring (96), using theoretical frequencies for HDO and D_2O, estimated the equilibrium constant for

$$H_2O + D_2O = 2HDO$$

as 3.26 at 298°K. and 3.40 at 373°K. for the gaseous state; they predict that these values will apply also to the liquid. Crist and Dalin (11) calculated equilibrium constants for

$$HDO + H_2 = H_2O + D_2$$

from 300° to 900°K. and also determined an experimental value of 0.66 at 800°K. Upon correction of an error in the first calculation the theoretical values became (12) 0.35 at 300°K., 0.62 at 525°K., and 0.83 at 900°K. This calculation is based upon that of Urey and Rittenberg (99) for H_2 and HD and upon Topley and Eyring's (96) frequencies for H_2O and D_2O. Crist and Dalin (13) showed that the system H_2–HD–D_2–H_2O–HDO–D_2O depends upon three equilibrium constants which may be taken as

$$H_2 + D_2 = 2HD$$
$$D_2O + H_2 = H_2O + D_2$$
$$HDO + H_2 = H_2O + HD$$

The first and third of these had been calculated previously. Crist and Dalin calculated the second also, finding 0.2 at 373°K. and 0.606 at 800°K. They present curves giving the equilibrium concentrations of all six constituents as a function of the ratio D/(H + D) for the special case

$$(H_2) + (HD) + (D_2) = (H_2O) + (HDO) + (D_2O)$$

at 373° and 800°K. The calculated results at the higher temperature were shown to agree with experimental values.

Chlorine, Cl^{35} and Cl^{37}. Giauque and Overstreet (30) tabulate $-F/T$ for the normal isotopic mixture.

Chlorine, Cl_2^{35}, $Cl^{35}Cl^{37}$, and Cl_2^{37}. Giauque and Overstreet (30) calculated $-F/T$ for each of these molecules from 250° to 3000°K. They showed that at 298°K. the equilibrium constant for

$$Cl_2^{35} + Cl_2^{37} = 2Cl^{35}Cl^{37}$$

was 3.9997, against the value 4, which would correspond to no preference among the three types of molecules. They interpreted this close agreement to mean that no isotopic separations would occur to an appreciable extent at 298°K. or higher temperatures. They, therefore, combined the three $-F/T$ values to a weighted average "practical" $-F/T$ from which nuclear spin and mixing effects are excluded; they discuss in detail the use of such practical functions. It may be seen, however, that this averaging process is not allowable when the highest accuracy is desired. Thus one can calculate from the data given by Giauque and Overstreet[5] that $-\Delta F/T = 0.012$ and $K = 1.006$ for

$$Cl_2^{35} + 2HCl^{37} = Cl_2^{37} + 2HCl^{35}$$

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[5] In making this calculation, it should be noted that the astonishing figures given by Giauque and Overstreet for the zero-point energies of the Cl_2^{35}, $Cl^{35}Cl^{37}$, and Cl_2^{37} molecules, 800.46, 789.60, and 778.56 cm.$^{-1}$ are numerically correct, but are calories instead of cm.$^{-1}$

These authors failed to make this calculation, and thus failed to note the possibility of slight isotopic separation. When this separation is not important, the weighted averages may be used.

Giauque and Overstreet (30) used their $-F/T$ values and a spectroscopic ΔE_0 of 56,900 cal. to calculate $\Delta F/T$ for

$$Cl_2 = 2Cl$$

from 250° to 3000°K. Spencer and Justice (93) calculated the specific heat from 300° to 1500°K. and gave an empirical equation to fit their values.

Urey and Greiff (98) calculated the ratio of f values for Cl_2^{37} and Cl_2^{35}.

Chlorine dioxide, ClO_2^{16} *and* ClO_2^{18}. The three fundamental frequencies of ClO_2^{16} are known from the work of Ku (67), but there is some uncertainty as to the shape of the molecule; the more probable value for the angle O—Cl—O is 65°, but 121° 20′ is not excluded. Using both sets of constants and theoretical isotope shifts, Urey and Greiff (98) calculated the f ratio, and found for the equilibrium constant of

$$ClO_2^{16} + 2H_2O^{18}(g) = ClO_2^{18} + 2H_2O^{16}(g)$$

the values 1.021, 1.015 at 298°K.

Hydrogen chloride, HCl^{35} *and* HCl^{37}. Giauque and Overstreet (30) gave $-F/T$ for HCl^{35}, HCl^{37}, and the equilibrium mixture, and $\Delta F/T$ for

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Cl_2 = HCl$$

from 250° to 3000°K. In calculating $\Delta F/T$ they used the value $\Delta F_{298.1} = -22{,}741$ cal. obtained by Randall and Young (84) from electromotive force measurements, corresponding to $\Delta E_0 = -21{,}984$ cal. Rossini (91) found the calorimetric value $\Delta H_{298.1} = -22{,}063 \pm 12$ cal., giving $\Delta E_0 = 22{,}019 \pm 12$ cal. He assigns an uncertainty of 33 cal. to the Randall and Young value, arising almost entirely from the step

$$HCl(aq) = HCl(g)$$

A slight revision of Giauque and Overstreet's $\Delta F/T$ values is thus perhaps desirable. Giauque and Overstreet also calculated $S_{298.1}$ more accurately than Giauque and Wiebe (31) had done, finding 44.658 (with entropy of mixing and of nuclear spin excluded) against the latter workers' experimental third law value of 44.5. Spencer and Justice (93) calculated C_p from 300° to 1500°K. and gave an empirical equation to fit their results. Urey and Greiff (98) calculated f ratios for HCl^{37} and HCl^{35} and K for

$$Cl_2^{35} + 2HCl^{37} = Cl_2^{37} + 2HCl^{35}$$

Deuterium chloride, DCl^{35}. Urey and Rittenberg (99) used theoretical spectroscopic relations to obtain energy levels of DCl^{35} from those of HCl^{35};

they calculated $-F/T$ for DCl^{35} from 200° to 700°K. Since they used a slightly different energy formula for HCl^{35} than that adopted by Giauque and Overstreet, and also a slightly different value of R, they calculated also the corresponding consistent values for HCl^{35}. They thus obtained the following values for K of

$$H_2 + 2DCl^{35} = D_2 + HCl^{35}$$

T	0°	200°	298.1°	400°	575°	700°K.
K	0.000	0.309	0.502	0.647	0.807	0.874

Atomic bromine, Br. $-F/T$ has not been tabulated explicitly, but dissociation constants are given below.

Bromine, Br_2. Gordon and Barnes (43) have calculated $-F/T$, S, and C_p from 200° to 1600° K., using the spectroscopic constants for $Br^{79}Br^{81}$. They show that this is equivalent within their limit of error to weighting the separate isotopic varieties as Giauque and Overstreet (30) did for chlorine. They calculated the equilibrium constant for

$$Br_2 = 2Br$$

using the accurate spectroscopic value $\Delta E_0 = 45{,}230$ cal. given by Brown (6). The experimental values of $R \log K$ given by Bodenstein (5) are about 0.5 cal. per degree less than the calculated values. It has been suggested to the writer (89) that this discrepancy may indicate the formation of Br_3. Spencer and Justice (93) have given an empirical equation to fit the C_p values of Gordon and Barnes. Urey and Greiff (98) calculated f ratios for Br_2^{81}, Br_2^{79}.

Hydrogen bromide, HBr^{79} and HBr^{81}. Giauque and Wiebe (32) calculated $S_{298.1}$, finding 47.53 as against their third law value of 47.6. This calculated value was revised subsequently (33) to 47.48. Gordon and Barnes (43) calculated $-F/T$, S, and C_p from 200 to 1600°K.; they give $S_{298.1} = 47.481$. They also calculated K for

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}Br_2 = HBr$$

using a calorimetric heat of reaction. Spencer and Justice (93) have given an empirical equation to fit the above C_p values. Urey and Greiff (98) calculated f ratios for HBr^{81} and HBr^{79}, and found K for

$$Br_2^{79} + 2HBr^{81} = Br_2^{81} + 2HBr^{79}$$

The values of 1.001 at 273°K., 1.0008 at 298°K. and 0.99994 at 600°K. effectively discourage the use of isotopic exchange reactions to separate isotopes of elements with large atomic weights.

Iodine, I_2. Gibson and Heitler (34) used the spectroscopic values for I_0, ω_0, and D, with a slight anharmonic correction not clearly explained, to calculate K for

$$I_2 = 2I$$

from 1073° to 1473°K. Their results agree to within less than 1 per cent with experimental values of Starck and Bodenstein (94). Giauque (26) calculated $S_{298.1} = 62.29$ for I_2 gas at 1 atm. He combined spectroscopic data with accurate vapor pressure measurements to obtain $\Delta E_0 = 15{,}640 \pm 3$ cal. for

$$I_2(s) = I_2(g)$$

Hydrogen iodide, HI. Giauque and Wiebe (33) calculated $S_{298.1} = 49.4$, using the spectroscopic moment of inertia but assuming a rigid molecule, owing to lack of sufficient data; their third law value was 49.5.

Deuterium iodide, DI. Urey and Rittenberg (99), likewise handicapped by insufficient data, calculated the following K values for

$$H_2 + 2DI = D_2 + 2HI$$

T	0°	298.1°	400°	575°	700°K.
K	0	1.164	1.212	1.234	1.222

These values were confirmed experimentally by Rittenberg and Urey (87).

Iodine chloride, ICl. McMorris and Yost (77) calculated from spectroscopic data $S_{298.1} = 59.2$; by combination of this value with the values $S_{298.1} = 62.29$ for $I_2(g)$ and $S_{298.1} = 53.31$ for Cl_2 given by Giauque, and with a spectroscopic ΔE_0 they find

$$-\Delta F/T = 3461/T + 1.40$$

for

$$\tfrac{1}{2}I_2(g) + \tfrac{1}{2}Cl_2 = ICl$$

They quote a more recent calculation by Brown, according to which $S_{298.1}$ for ICl is 59.15 and $-\Delta F/T = 3280/T + 1.36$.

Sulfur, S. $-F/T$ values have been tabulated by Montgomery and Kassel (79) from 250° to 5000°K.

Sulfur, S_2. Montgomery and Kassel (79) calculated $-F/T$ from 250° to 5000°K. If the reinterpretation of the underlying spectroscopic data suggested by Badger (2) is accepted, these values must be increased by 0.55, as was shown by Cross (14). Montgomery and Kassel also gave $\log_{10} K$ for

$$S_2(g) = 2S$$

These values must be decreased by 0.120 to take care of the above correction. Cross calculated $S_{298.1} = 54.417$.

Sulfur monoxide, SO. Montgomery and Kassel (79) calculated $-F/T$ for SO and by the use of an accurate spectroscopic energy of dissociation and of Johnston and Walker's (57) values of $-F/T$ for O_2, uncorrected for the $^1\Delta$ state, calculated $\log_{10} K$ for

$$\tfrac{1}{2}S_2(g) + \tfrac{1}{2}O_2 = SO$$

These values must be decreased by 0.060 to take account of the changed values for S_2, and by 0.002 at 2000°, 0.015 at 3000°, 0.038 at 4000° and 0.065 at 5000°K. for the $^1\Delta$ level.

Sulfur dioxide, SO_2^{16} and SO_2^{18}. Gordon (39) calculated $-F/T$ for sulfur dioxide from 298° to 2800°K., using somewhat incomplete spectroscopic data. He obtained ΔE_0 for

$$\tfrac{1}{2}S_2(g) + O_2 = SO_2$$

from a combination of spectroscopic calculations with calorimetric data for

$$S_{rh} + O_2 = SO_2$$

and

$$S_{rh} + H_2 = H_2S$$

and thus calculated K for the first reaction above. He used the SO values of Montgomery and Kassel (79) as revised by Cross (14) and the O_2 values of Johnston and Walker (57) uncorrected for the $^1\Delta$ level, to calculate K for

$$SO + \tfrac{1}{2}O_2 = SO_2$$

Urey and Greiff (98) calculated the f ratio for SO_2^{18} and SO_2^{16}.

Hydrogen sulfide, H_2S. Cross (14) used incomplete spectroscopic data to calculate $-F/T, S, C_p$ from 212.77° to 1800°K. Comparison of spectroscopic values with equilibrium measurements gives for

$$H_2S(g) = H_2 + \tfrac{1}{2}S_2(g)$$

the precise value $\Delta E_0 = 19620 \pm 30$ cal.

Nitrogen, N. $-F/T$ values have been tabulated up to 5000°K. by Giauque and Clayton (28).

Nitrogen, N_2^{14}. Giauque and Clayton (28) calculated $-F/T$ to 5000°K. and also $S_{298.1} = 45.788$ excluding the nuclear spin entropy $R \log 9$. The experimental value is 45.9. The agreement shows that ortho- and paranitrogen are present in the solid state at low temperatures in the high-temperature proportion of 6:3, but that the paranitrogen is present in the solid in a form carrying only the spin weight of 3. There are then nine forms present in the solid in equal quantities, giving a contribution R log 9 to the entropy which does not appear in the specific heat measurements; since this is just equal to the excluded spin entropy, the third law value agrees with the spectroscopic one. If the paranitrogen molecules were rotating in the crystal, they would have an extra weight factor of 3; the unmeasured entropy of the solid would then be $2/3\ R \log 9 + 1/3\ R \log 27 = R \log 9 + 1/3\ R \log 3$, and the third law value would be 0.7 cal. per degree less than the spectroscopic value.

Giauque and Clayton made a tentative calculation of K for

$$N_2 = 2N$$

based on $\Delta E_0 = 182{,}000$ cal. This value is still uncertain.

Johnston and Davis (52) gave a curve showing C_p for the ortho, para, equilibrium, and non-equilibrium mixtures up to 20°K. They have tabulated C_p and S from 50° to 5000°K., and H from 100° to 5000°K. Spencer and Justice (93) fitted an empirical equation to these C_p values.

Nitrogen, N_2^{15}. Urey and Greiff (98) calculated the ratio of f values for N_2^{15} and N_2^{14}.

Nitric oxide, NO. Johnston and Giauque (54) calculated $S_{121.36} = 43.75$, and interpolation of the later calculations of Johnston and Chapman gives $S_{121.36} = 43.753$. Johnston and Giauque found an experimental value of 43.0 from specific heat measurements. The discrepancy of $0.75 \sim R/2 \log 2$ was explained by them as due to the existence in the solid of two forms of N_2O_2 differing in coupling. Later Blue and Giauque (4) proposed that the extra entropy in the solid arises from two different orientations of a single kind of N_2O_2. Johnston and Chapman (50) calculated $-F/T$ from 50° to 5000°K., S from 1° to 5000°K., and C_p from 0.5° to 5000°K. A numerical error in the value of $-F/T$ at 1125°K. was corrected subsequently (51). Witmer (108) pointed out an error by Johnston and Chapman in interpretation of the spectroscopic data and gave revised tables for C_p, S, and $-F/T$ from 1° to 500°K.; at higher temperatures the error produces a negligible effect on the calculated thermodynamic functions. Johnston and Chapman used the estimate $\Delta E_0 = 142{,}000$ cal. to calculate approximate values of K for

$$NO = N + O$$

Giauque and Clayton (28) used their own $-F/T$ for N_2, those of Johnston and Chapman for NO, those of Johnston and Walker (57) uncorrected for the $^1\Delta$ level for O_2 and unusually concordant calorimetric data of Thomsen and Berthelot equivalent to $\Delta E_0 = 21{,}400$ cal. to calculate K for

$$\tfrac{1}{2}N_2 + \tfrac{1}{2}O_2 = NO$$

from 298° to 5000°K. These values must be considered provisional until a more certain value of ΔE_0 is available.

Nitric oxide, $N^{15}O$. Urey and Greiff (98) calculated K for

$$N_2^{14} + 2N^{15}O = N_2^{15} + 2N^{14}O$$

Nitrous oxide, N_2O. Kassel (64) used spectroscopic data which gave the anharmonic constants, but not the probably less important rotational stretching correction, to calculate $-F/T$, H, and C_p from 250° to 1500°K. Recent calorimetric data for the reaction

$$N_2 + \tfrac{1}{2}O_2 = N_2O$$

give $\Delta E_0 = 20{,}429$ cal. The equilibrium constant then was calculated as 6.87×10^{-19} at 300°K., 6.87×10^{-9} at 1000°K., and 1.98×10^{-7} at 1500° K., on the basis of Giauque and Clayton's (28) data for N_2 and Johnston and Walker's (57) data for O_2, uncorrected for the $^1\Delta$ level.

Kassel gave $S_{298.1} = 52.575$ with nuclear spin excluded. Blue and Giauque (4) calculated 52.581. Previous less accurate calculations had been made by Badger and Woo (3), who found 52.58, and by Rodebush (88), who used an incorrect moment of inertia. Blue and Giauque's experimental third law value is 51.44, 1.14 lower than the calculated value. If in the actual crystal at the lowest temperatures reached the orientations NNO and ONN occurred at random, the crystal would possess an entropy $R \log 2 = 1.377$ which would have to be added to $\int (C_p/T)dT$. The discrepancy is slightly less than this, a fact which may be taken to indicate a partial orientational ordering.

Ammonia, NH_3. No extensive calculations have been made for ammonia. An old controversey involving Villars (102), Giauque, Blue and Overstreet (27), and MacDougall (75) with regard to the entropy need not be revived now. The absolute $S_{298.1}$ is 52.10; with all nuclear spin excluded the "virtual" entropy is 45.79. One or the other of these values should be used in all calculations.

Bryant (7) has given an empirical equation to fit his approximate spectroscopic C_p values from 300° to 2000°K.

Carbon, C. By integrating experimental heat-capacity data, Clayton and Giauque (9) have calculated $-F/T$ for β-graphite from 250° to 3000°K. These are not spectroscopic values, of course, but are included here for convenience.

Carbon monoxide, $C^{12}O^{16}$, $C^{13}O^{18}$, and $C^{12}O^{18}$. Clayton and Giauque (9) calculated $-F/T$ for CO to 5000°K.; they later (10) published a revised table, as the first had been based on an incorrect energy level equation. They gave $S_{298.1} = 47.316$; the experimental third law value was 46.2. The difference of 1.1, slightly less than $R \log 2 = 1.38$, was considered to indicate an almost random distribution as between CO and OC in the crystal, with a slight preference for regularity. They used heats of combustion of graphite and of carbon monoxide to calculate equilibrium constants for

$$C\ (\beta\text{-graphite}) + \tfrac{1}{2}O_2 = CO$$

up to 3000°K. These calculations, owing to the uncertainties in $-F/T$ and the heat of combustion for graphite, were not considered worth revising along with the $-F/T$ values for CO. Kassel (63) calculated the other thermodynamic functions for CO, using Giauque's original incorrect energy equation. Johnston and Davis (52) used correct data to calculate C_p and S from 50° to 5000°K. and H from 100° to 5000°K. Spencer and Justice (93) gave an equation to represent these C_p values. Urey and Greiff (98) calculated f ratios for $C^{13}O$, $C^{12}O$ and for CO^{18}, CO^{16}, and K for

$$C^{12}\ (\beta\text{-graphite}) + C^{13}O = C^{13}\ (\beta\text{-graphite}) + C^{12}O$$
$$CO^{16} + H_2O^{18} = CO^{18} + H_2O^{16}$$
$$2CO^{16} + O_2^{18} = 2CO^{18} + O_2^{16}$$

Carbon dioxide, $C^{12}O_2^{16}$, $C^{12}O_2^{18}$, and $C^{13}O_2^{16}$. Approximate calculations for CO_2 were made by Gordon and Barnes (40) and Gordon (35). Kassel (64) later used more complete data to calculate accurate values for $-F/T$, H, and C_p up to 1500°K. and somewhat uncertain estimates up to 3500°K. He used the data of Clayton and Giauque (9) on C, their revised data (10) on CO, the data of Giauque (25) and of Davis and Johnston (15) on H_2, of Johnston and Walker (57) on O_2, and of Gordon (36, 37) on H_2O, together with precision heats of combustion, to calculate equilibrium constants for

$$2CO_2 = 2CO + O_2$$
$$CO_2 + C = 2CO$$
$$CO_2 + H_2 = CO + H_2O$$

The values for the water gas equilibrium agree well with the best experimental values. Those for the producer gas reaction suggest a "zero-point" entropy of 0.5 cal. per degree for graphite, as had been pointed out by Gordon (35).

Urey and Greiff (98) calculated f ratios for CO_2^{18}, CO_2^{16} and for $C^{13}O_2$,

$C^{12}O_2$, and K values for

$$CO_2^{16} + 2H_2O^{18}(g) = CO_2^{18} + 2H_2O^{16}(g)$$
$$CO_2^{16} + CO_2^{18} = 2CO^{16}O^{18}$$
$$C^{13}O + C^{12}O_2 = C^{12}O + C^{13}O_2$$
$$C^{12} + C^{13}O_2 = C^{13} + C^{12}O_2$$

Methane, CH_4. Approximate values of $-F/T$ up to 5000°K. were calculated by Kassel (60a) and used to obtain K for

$$C\ (\beta\text{-graphite}) + 2H_2 = CH_4$$

Vold (105) used essentially the same data to calculate C_p from 273° to 773°K.

Acetylene, C_2H_4. Kassel (60a) calculated $-F/T$ to 3000°K. and also K for

$$2C\ (\beta\text{-graphite}) + H_2 = C_2H_2$$

These later values are considerably in doubt, owing to the uncertain heat of combustion of acetylene.

Ethylene, C_2H_4. Kassel (60a) used very imperfect spectroscopic data to estimate $-F/T$ for ethylene and K for

$$2C\ (\beta\text{-graphite}) + 2H_2 = C_2H_4$$

up to 3000°K. He also calculated C_p at 300° and 350°K. Smith and Vaughan (92) calculated S and H from 298° to 973°K. and C_p from 143° to 464°K., using somewhat different frequencies than those given by Kassel; these frequencies were chosen in such a way as to give improved agreement with the experimental values of C_p.

Ethane, C_2H_6. Smith and Vaughan (92) used frequencies given by Eucken and Parts (21) as follows: 712 cm.$^{-1}$ (2), 826 (2), 990 (1), 1460 (2), 1465 (2), 1499 (2), 2975 (6), the multiplicity being indicated in parentheses. The 712 and 826 cm.$^{-1}$ frequencies have no appreciable support from spectroscopic work, but give low temperature C_p values in agreement with Eucken and Parts experiments. Smith and Vaughan calculated C_p from 143° to 373.5°K. and S and H from 298° to 973°K. They then calculated K for

$$C_2H_6 = C_2H_4 + H_2$$

The calculated values are larger than the experimental, the excess in $R \log K$ being about 1.2 cal. per degree. They made an error in calculating the largest moment of inertia of ethane from interatomic distances; when this error is corrected the discrepancy is increased by 0.27 cal. per degree. As was pointed out in an earlier section, ethane has an internal "free rotation." Smith and Vaughan are inclined to ascribe this disagreement to lack of freedom in that rotation.

Paraffins, C_nH_{2n+2}. Very rough, approximate values for $-F/T$, H, S, and C_p for the normal paraffins from ethane through hexane will be published by the author in the near future.

Chloromethanes, CH_3Cl, CH_2Cl_2, $CHCl_3$, and CCl_4. Vold (105) used incomplete data to calculate C_p from 273° to 773°K.

Hydrogen cyanide, HCN. Badger and Woo (3) calculated $S_{298.1}$ = 48.23 exclusive of nuclear spin entropy. Bryant (7) calculated the specific heat and gave an approximate equation.

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THERMODYNAMIC ASPECTS OF THE THEORY OF NON-ELECTROLYTIC SOLUTIONS

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I wish to discuss several of the important steps in the development of the theory of solutions of non-electrolytes with special reference to their thermodynamic corollaries. We will begin, of course, with the mention of Raoult's law. This rests historically upon an experimental foundation; however, its theoretical basis is now clear and so simple that anyone should be able to understand it and to see the conditions under which actual systems should approximate thereto (6, 15, 23). Its thermodynamic implications have, for the most part, been thoroughly set forth. There is only one minor, but nevertheless interesting, addition I wish to make here. If the partial vapor pressure of a component of a binary mixture is expressed as proportional to its volume concentration instead of its mole fraction, as in Raoult's law, the application of the Gibbs equation[1] connecting the partial molal free energies of the two components of a mixture shows that the molal volumes of the two components must be equal, in which case the volume concentration reduces to the mole fraction of Raoult's law. This means that volume concentration can satisfy the Gibbs equation only in the special case that it is identical with mole fraction, whereas the latter is always consistent therewith.

Earlier attempts to treat concentrated solutions on the basis of osmotic pressure formulae have been abandoned (1, 8, 14, 19) by all who have taken the trouble to inform themselves regarding the more adequate methods now available.

The majority of systems do not satisfy the condition of equal molecular fields required for obedience to Raoult's law and a more general treatment is necessary. The success of van der Waals in setting up an approximate equation of state naturally invited its extension to mixtures. The energy of a mixture of $n_1 + n_2$ moles according to this theory should be given by the expression $(n_1^2 a_1 + 2n_1n_2a_{12} + n_2^2 a_2)/(n_1b_1 + n_2b_2)$, where a and b are the usual "constants" of the van der Waals equation, the subscripts referring to the pure components and the mixture, respectively. This was applied by van Laar (19, 20, 21) to yield the following expression for the partial vapor pressure of a component of a binary solution.

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[1] This equation is usually known as the Duhem-Margules Equation, but should be credited to Gibbs, unless special forms of it are regarded as worthy to bear another name.

$$RT \ln (p_1/p_1^0\mathrm{N}_1) = \alpha\mathrm{N}_2^2/(1 + r\mathrm{N}_2)^2$$

where

$$\alpha = (a_1b_2^2 - 2a_{12}b_1b_2 + a_2b_1^2)/\mathrm{b}_1^3$$

and

$$r = (b_2 - b_1)/b_1$$

Sometimes v_1 and v_2 were substituted for b_1 and b_2, respectively. (Actually v is often 25 per cent greater than b.) The "derivation" of this equation is not easy to follow; some of the steps seem to be assumed rather than derived, and the molal volume is interchanged *ad libitum* with the "constant" b; the notation is not always clearly defined and moles and mole fractions are not clearly distinguished. The derivation was patched up and presumably improved, however, each of the many times it was repeated in the series of papers. Experimental tests were fragmentary and usually confined to citing systems which show qualitative agreement with the theory. It was concluded that equality of critical pressures was the criterion for ideal behavior of a solution. This is not only comparatively useless but often untrue. Anyone familiar with the shortcomings of the van der Waals equation for a pure substance could hardly feel great confidence in the validity of this treatment by van Laar in which good thermodynamics was scrambled intimately with an inadequate equation of state. The result turned out far better than could be expected, as we shall show later.

Dolezalek (3) and many others have attributed all deviations from Raoult's law to "chemical" changes alone—association and solvation—but although such equilibria often exist it is just as naïve to attribute all deviations to this cause as it would be to attribute all deviations from the perfect gas laws to chemical equilibria to the neglect of non-valence intermolecular forces and the effects of molecular volumes.

The above equation of van Laar simplifies to

$$RT \ln \gamma_1 = \alpha\mathrm{N}_2^2$$

in the special case that $b_1 = b_2$ (or $\mathrm{v}_1 = \mathrm{v}_2$). We have substituted the activity coefficient, γ_1, for $p^1/p_1^0\mathrm{N}_1$. This equation was also derived by Heitler (5) without the aid of an equation of state, by assuming the structure of the liquid to be a simple cubic lattice in which the two molecular species are interchangeable. The term N_2^2 arises from a consideration of the frequency with which adjacent molecules are made up of the respective combinations, 1–1, 1–2, and 2–2. This derivation is not as convincing as it would be if it did not depend upon a model so highly artificial and did not involve the assumption that the volumes of the two molecular species are equal.

Work has proceeded in our laboratory over a period of years to amass experimental data involving non-polar, symmetrical molecules having molecular fields of widely different strength, as indicated by various criteria. It was soon evident that, in the absence of specific valence or polar forces, differences in the field strengths or "internal pressures" give rise to corresponding positive deviations from ideal solubility relations. Moreover, there was an unmistakable regularity of behavior as shown by the temperature coefficients of the solubility curves for many of these highly imperfect or non-ideal solutions. The explanation suggested itself that in these solutions the thermal agitation is sufficient to overcome the segregating effect of unequal molecular fields and give, at least approximately, the same randomness of mixing as would exist in an ideal solution, where the molecular fields are equal. The interpretation of randomness in terms of entropy suggested that the above statement might be formally expressed as $\bar{S}_1^r = \bar{S}_1^i$ when $N_1^r = N_1^i$, that is, the partial molal entropy of a component of a regular solution is the same as it would be in an ideal solution of the same composition. The latter is known, being given by

$$\bar{S}_1^i = -R \ln N_1$$

There are a number of interesting thermodynamic consequences of this definition which have been set forth elsewhere (7).

Scatchard (18) utilized this concept, together with a certain formulation of the "cohesive energy" of a mole of mixture, to arrive at a formula without involving the van der Waals equation. He says, "For non-ideal solutions also we shall neglect the change in volume and we shall consider only the case in which the interaction between any pair of molecules is independent of the composition. We may then split the cohesive energy of a mole of the mixture in the following way

$$u_x = (a_{11}v_1^2x_1^2 + 2_{12}av_1v_2x_1x_2 + a_{22}v_2^2x_2^2)/(v_1x_1 + v_2x_2)$$

where the a's are constants" (and the x's mole fractions). "For the pure components $u_1 = a_{11}v_1$ and $u_2 = a_{22}v_2$, so that a_{11} and a_{22} are the cohesive energy densities of the components." The a's in this formulation are not, of course, constant over a range of temperature, but merely characteristic functions of each liquid at a given temperature. They are not the van der

Waals a's, which are, theoretically at least, given by the relation $u = a/\mathrm{v}$, so that $\mathrm{a} = a/\mathrm{v}^2$. If we make this substitution in the above equation, we arrive at the same formula used by van Laar.

Meanwhile, we have been endeavoring to make a more rigorous study of the problem on a statistical basis. The method of Heitler was extended to cover any lattice arrangement in connection with a problem involving molten salt solutions (10). The "probability function," W, used by Prins (17), Zernike (24), and Debye and Menke (2, 16; see also 13) to express the structure of a liquid in terms of radial distribution then supplied the means for extending the proof to liquids, yielding the equation (11)

$$\Delta E' = \frac{2\pi N^2}{\mathrm{v}}\left[n_1^2 \int W_{11}\epsilon_{11}r^2\mathrm{d}r + n_2^2 \int W_{22}\epsilon_{22}r^2\mathrm{d}r + 2n_1n_2 \int W_{12}\epsilon_{12}r^2\mathrm{d}r\right]$$

where N is the Avogadro number and the ϵ's are the intermolecular potentials. In the absence of more exact knowledge of some of its terms certain assumptions had to be made in order to subject it to certain experimental verification, the results of which, however, have turned out to be remarkably satisfactory (9). The simplified approximation formula is

$$RT \ln \gamma_1 = \mathrm{v}_1\left\{\frac{\mathrm{N}_2\mathrm{v}_2}{\mathrm{N}_1\mathrm{v}_1 + \mathrm{N}_2\mathrm{v}_2}\right\}^2 \left\{\left(\frac{\Delta\mathrm{E}_1}{\mathrm{v}_1}\right)^{\frac{1}{2}} - \left(\frac{\Delta\mathrm{E}_2}{\mathrm{v}_2}\right)^{\frac{1}{2}}\right\}^2$$

which, surprisingly enough, turned out to be identical with the formula of van Laar, provided v's are used in place of b's and $\Delta\mathrm{E} = a/\mathrm{v}$. The term, $\Delta\mathrm{E}$, denotes energy of vaporization, N is mole fraction, and γ the activity coefficient referred to the pure liquid as the standard state.

Guggenheim (4) has recently published an interesting paper on the subject of the statistical mechanics of regular solutions. He defines a regular solution as follows: "For the sake of simplicity we shall consider a mixture of two species 'A' and 'B'. The extension to mixtures of more than two species will be obvious. In our model of a regular solution we postulate first the absence of long-range (electrostatic) forces between the molecules. Our second assumption is that the 'A' and 'B' molecules may be treated as spheres of at least approximately the same size. Thirdly, we assume that each molecule whether of 'A' or 'B' is directly surrounded by the same number r of other molecules. If the molecules are closely packed, r will have the value 12, but for our present purpose, there is no need to assign any specified value to r, provided its value is the same for the 'A' molecules as for the 'B' molecules. Fourthly, we assume that the liquids 'A' and 'B' mix in all proportions without volume change. Our fifth assumption is that, for varying configurations (all of the same volume) of the system, the total potential energy may be regarded as the sum of contributions of each pair of molecules in direct contact. This assumption is slightly less drastic than assuming that the field of a given molecule does not extend beyond the further side of the next molecule. It is equivalent to ignoring differences between the field of an 'A' molecule and that of a 'B' molecule at distances exceeding one molecular diameter. Obviously our first assumption is included in our fifth."

I should like to utter a good-natured complaint, first of all that he should adopt a term which I invented and defined in a certain way but should give it a different and restricted definition. He practically rules out all solutions whose components have significantly different molecular radii. It is, of course, easy to see why a "statistical mechanic" or "mechanical statistician," whichever one should be called, should wish to confine his attention to molecules of equal size. The problems of statistical distribution of checkers on an ordinary checker-board are very simple, but suppose that the two sets of checkers were not only of unequal size but required the squares on the board to change size to accommodate them as they move; the statistics of such a checker-board would be rather baffling. It would be still worse if one of the players would use sausages, corresponding to paraffin molecules, in place of checkers.

Using the simple model he sets up it is, perhaps, not surprising that he should state that the volume fraction in the formula used by Scatchard and by myself "must be regarded as purely empirical." Even if the derivation is not convincing, the experimental evidence is all in favor of the volume fraction occurring in the formula. Many examples of this will be given in the second edition of my monograph on "Solubility" now in press and I need give here only one sample. The molal volumes of liquid cadmium and lead at 432°C. are 14.2 cc. and 19.1 cc., respectively. The values of the excess partial molal free energy of cadmium in the actual over the ideal solution should give a constant, according to our equation, when divided by the square of the volume fraction, v_2^2, rather than the mole fraction, N_2^2, of the lead. The following brief table for widely different compositions shows that this is the case.

N_1	$\frac{\bar{F}_1 - \bar{F}_1^i}{v_2^2}$	$\frac{\bar{F}_1 - \bar{F}_1^i}{N_2^2}$
0.696	1800	2790
0.401	1760	2180
0.123	1820	1960

A much more important criticism by Guggenheim is to the effect that in the presence of unequal molecular fields the completely random distribution postulated in my definition of a regular solution cannot persist, but will give rise to some approach to the eventual segregation into two liquid phases as the temperature is lowered and the thermal agitation falls off. To take this tendency into account he defines and evaluates a certain quantity, $\bar{x}$, expressing departure from randomness. He then sets up a semi-empirical expression,

$$\bar{x}^2 = (N_1 - \bar{x})(N_2 - \bar{x})e^{-2\lambda/rkT}$$

which cleverly introduces the exponential, which is undoubtedly a step in the right direction. Here $2\lambda/r$ is the "work required to change a 1–1 pair and a 2–2 pair into two 1–2 pairs, and N_1 and N_2 denote the numbers of molecules. This takes account of the fact that there will be departures from random mixing favoring contact between molecules with low mutual potential energy."

On the basis of this formulation, he sets up the following expression, using our notation, with n denoting number of moles and N the Avogadro number, for the free energy of mixing,

$$\Delta F = \frac{n_1 n_2}{n_1 + n_2} N\lambda \left\{1 - \frac{2n_1 n_2}{(n_1 + n_2)^2} \cdot \frac{2N\lambda}{rRT}\right\}$$

(The original contains an error in omitting to square the second $n_1 + n_2$.) He points out the effect of values of $2\lambda/rkT$ approaching unity and states that the "application by Hildebrand and others" of a formula omitting this factor "to two liquids that are incompletely miscible is particularly unwarranted." His final conclusion is that "the semi-empirical formulae proposed by Hildebrand and other authors are inconsistent with the principles of statistical mechanics."

Now no one can deny that any differences in molecular field strength will introduce a tendency towards segregation which must prevent the partial molal entropy being strictly equal to its value in an ideal solution of the same composition. The only question is, are the departures sufficient to vitiate the simple conclusions one can draw from equating free and total energy. I am indebted to Professor Linus Pauling, with whom the matter was discussed, for suggesting a simple but striking test of the matter. We may calculate ΔF by means of the above equation, assuming it to be correct, and note the magnitude of the correcting term in the bracket. If we set $r = 12$, $T = 300$, and $\lambda = 1800$ cals., we find that ΔF is 394 cals., at $n_1 = n_2 = 0.5$, with the bracketed term 0.875 instead of 1.000, i.e., the correction amounts to 12.5 per cent, although the deviation from Raoult's law is large; the activity would be nearly 100 per cent greater than the ideal in the 50 mole per cent solution having this value of ΔF. Moreover, the correction is greatest at this composition, falling off rapidly in either direction, e.g., it is but 4.5 per cent in a 10 mole per cent solution. The discrepancy for most systems in the range of interest would thus be at least as small as the other sources of uncertainty. The greatest effect would occur in the neighborhood of the critical solution temperature; an experimental measure of its magnitude will be possible by comparing the shape of the actual solubility curve in this region with its course elsewhere. This point was briefly discussed in the paper by myself and Wood.

The analogous case of the critical behavior of a pure substance is enlightening. If a gas is compressed at a temperature well below its critical temperature there is very little departure from the behavior of a perfect gas as the saturation pressure is reached, and even this can be well accounted for by a simple equation of state without introducing the picture of clustering, i.e., the molecular arrangement is random. The pure condensate also possesses a random molecular arrangement, unaffected by the presence of the gaseous phase. On the other hand, if the gas is compressed at, say, one degree below the critical temperature, the clustering is clearly visible to the naked eye. The size of these clusters changes, however, very rapidly with temperature, in such a way as to indicate their practical disappearance not many degrees away from the critical point in either direction. The behavior of a liquid solution should be similar. If a little of X_2 is dissolved in much X_1, having a very different internal pressure, the molecules of the former will have a random distribution, in spite of the large difference in intermolecular potentials. If the temperature is well below the critical solution temperature, a second liquid phase will appear as more X_2 is added in which X_1 is dilute in X_2 and likewise randomly distributed. Only if the temperature is such that the system passes near the critical point as the composition is altered should there be much of the segregation due to an approximate balance of thermal energy and unequal molecular potentials.

It seems to me probable, therefore, that the assumption of completely random mixing will be found to hold nearly enough for most solutions of non-polar substances to serve the purpose of usefully approximate calculations. It may be doubted, further, whether statistical mechanics, in its present state of development, can be counted upon to give an answer to the question which is at once reliable and workable. Until so simple a problem as the entropy of vaporization shall receive a satisfactory statistical treatment, I am willing to run the risks of refusing to give up a method of attack which is supported by much experimental evidence simply because it is "inconsistent with the principles of statistical mechanics." I feel constrained, however, to reject this last objection of Professor Guggenheim entirely, because the probability functions in our general equation, expressing the structure of the solution, include the effect of segregation upon this structure whenever it can be adequately expressed, either upon an experimental or a theoretical basis. Even the effects of unsymmetrical fields or departures from spherical shape[2] can be expressed by suitable formulations of W.

Space does not permit a review of a recent noteworthy formulation by Kirkwood (12) of a comprehensive statistical treatment of fluid mixtures, in which the rather artificial model of Guggenheim is avoided.

Purported evidence for clustering in solutions of benzene with cyclohexane has been given by H. K. Ward (22) on the basis of x-ray scattering. Two distinct diffraction peaks shown by the solution corresponding to the pure liquids were interpreted as indicating a submicroscopic emulsion structure, regarded as the cause of the deviation of these solutions from Raoult's law. This interpretation would be more convincing, first, if a pair of liquids had been chosen whose diffraction peaks are separated by a large enough interval to afford more room for an intermediate peak,—the difference was only 0.41 A.U.; second, if the deviation from Raoult's law were not so small, in this case only 8.5 per cent at 79°C. for an equimolal solution. The study should be repeated using a solution of nonpolar liquids near their critical solution temperature.

The scope of this discussion does not suffice to include other interesting thermodynamic aspects of solubility theory that suggest themselves, such as the effect of volume changes upon the entropy and free energy of mixing; I wish merely to indicate that the subject is by no means exhausted and that there remain various interesting fields for research, both theoretical and experimental.

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[2] The original address included a brief discussion of some effects of hydrogen bond formation, which is here omitted in view of the fact that it is being written up more extensively for separate presentation (Science **83**, 21 (1936)).

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THE FREE ENERGY RELATIONS AMONG THE PARAFFIN AND OLEFIN HYDROCARBONS

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The application of thermodynamics to organic chemistry has been largely a development of the last decade. Up to a few years ago the lack of an adequate body of thermodynamic data pertaining to organic compounds constituted a discouraging factor. Now, however, over three hundred free energy values, representing many different types of substances, have been accumulated; and these results, while in many cases merely preliminary and semi-quantitative, serve as a very promising foundation for what we might term *thermodynamic organic chemistry.* Moreover at the present time new free energies, and more accurate ones, are being added to the literature at an accelerated pace.

One of the fields in which these new data have been recently obtained is that of the aliphatic hydrocarbons. In view of the recent developments in hydrocarbon chemistry, including especially the increasing use of cracking procedures and the utilization of olefins in organic syntheses, such data appear very timely and will undoubtedly aid in establishing thermodynamics as one of the important tools for further advances in aliphatic organic chemistry. The object of the present paper is to review, in the light of these new data, the free energy relations among the paraffins and olefins.

METHODS OF EVALUATING FREE ENERGY CHANGES AMONG THE HYDROCARBONS

In the present connection the term "free energy" of a hydrocarbon is used to denote the change in the free energy function of Lewis and Randall, i.e., the ζ function of Gibbs (14, 7), for the isothermal process in which a mole of the given hydrocarbon, either gaseous at 1 atmosphere pressure or in the liquid state as the case may be, is formed from graphitic carbon and the requisite amount of gaseous hydrogen, initially at 1 atmosphere pressure. For comparative purposes this free energy of formation from the elements has been calculated for the standard temperature of 298.1°K. (25°C.). In terms of the notation of Lewis and Randall, which is used throughout this paper, it is represented by the symbol ΔF^0_{298} in tables 1 and 3, although notice here should be taken of the fact that this symbol is a general one and naturally refers to any standard-state, isothermal process.

There are two methods by which the free energy changes in processes involving the hydrocarbons have been evaluated from experimental data. The first of these depends upon the determination of the equilibrium constant K in a reaction, whereby the free energy change for the standard-state reaction at the particular temperature is given by the equation

$$\Delta F^0_T = -RT \ln K \qquad (1)$$

This method has been used in studies of the formation of methane from the elements and of the production of various olefins by dehydrogenation of the corresponding paraffins at more or less elevated temperatures. However, it has its limitations in applicability because often the equilibrium constant cannot be readily determined experimentally and, of course, may be the very thing which one wishes to evaluate from a ΔF^0 value otherwise obtained.

The second method involves the use of the important thermodynamic relation

$$\Delta F^0 = \Delta H^0 - T\Delta S^0 \qquad (2)$$

and is quite generally applicable. The quantity ΔH^0, the change in "heat content" for the process, may sometimes be measured directly, as in the hydrogenation of various olefins, and in practically all cases may be evaluated indirectly from suitable combustion data by means of Hess's law. When the process of forming a hydrocarbon from the elements is under consideration, ΔS^0, the increase in entropy, represents the entropy of the hydrocarbon minus that associated with the requisite number of atoms of graphitic carbon and gaseous hydrogen. The entropy of the hydrocarbon may be evaluated from heat capacity data extending down to low temperatures by means of the third law of thermodynamics (16a) or in the simpler cases from spectroscopic data and molecular constants by statistical methods (4, 18). The entropy of graphitic carbon, 1.36 E.U. per gram-atom at 298°K., has been recently evaluated by means of the third law (9); the practical value, $S^0_{298} = 15.615$ E.U., for $\frac{1}{2}H_2$ was obtained by Giauque (5) in 1930 from spectroscopic data after subtraction of the effect for nuclear spin.

FREE ENERGY VALUES FOR SOME PARAFFIN HYDROCARBONS

The normal paraffins

The recent renaissance in thermochemistry has now made it possible to apply equation 2 to calculate fairly accurate values for the free energies of formation of eight members of the normal paraffin series. The results so obtained are given in the last column of table 1 and the essential thermal data involved in obtaining these are tabulated in columns 2, 3, and 4.

The ΔH^0_{298} values for all these paraffins save dodecane have been derived with the aid of the remarkably accurate heats of combustion measured recently by Rossini and his collaborators at the U. S. Bureau of Standards (19). The value for dodecane is based upon the combustion result of Banse and Parks (1), now corrected according to Washburn's method (23) to atmospheric pressure.

The molal entropies for these several hydrocarbons are given in column 3. The values above propane have all been obtained by Parks, Huffman, and collaborators (16b) from low temperature heat capacity data and the third law of thermodynamics. The highly accurate value for methane is that resulting from the statistical calculations of Giauque and coworkers and of Kassel (6, 10). The tabulated S^0_{298} for ethane is a mean based on the three approximate values (53.5, 55.5, and 56.2 E.U.), which have been calculated, respectively, by the third law by Parks and Huffman and by statistical methods by Mayer, Brunauer, and Mayer and by Smith and Vaughan (16b, 15, 21). The parenthetical value for propane is the result of a direct interpolation between ethane and *n*-butane. The marked regularities found in the entropies in the normal paraffin series would seem to make such an interpolation highly reliable.

TABLE 1

Thermodynamic data for some normal paraffins

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E. U.*	*E. U.*	*15°-calories*
Methane (g)	−18,070	44.46	−19.36	−12,300 (±80)
Ethane (g)	−20,600	55.0	−41.4	−8,260 (±300)
Propane (g)	−25,390	(64.7)	−64.3	−6,220 (±300)
n-Butane (g)	−30,570	74.4	−87.2	−4,580 (±300)
n-Pentane (l)	−42,230	62.0	−132.2	−2,820 (±500)
n-Heptane (l)	−55,410	78.5	−180.9	−1,480 (±500)
n-Octane (l)	−62,260	86.0	−206.0	−850 (±600)
n-Dodecane (l)	−85,910	118.2	−304.1	+3,540 (±1400)

The resulting free energies are subject to maximum fortuitous errors (indicated in parentheses in the last column of table 1) which are the cumulative effects of similar errors in the contributing combustion and entropy data. As Rossini has noted, there is also the possibility of a systematic error, perhaps as great as 100 calories per carbon atom, arising from the use of 94,240 cal.$_{15°}$ for the combustion of a gram-atom of β-graphite. To the reader these tabulated possible errors may seem rather large at first glance, especially in view of the extremely small values for the free energies of formation of the hydrocarbons. However, it should be remembered that in the practical use of free energy data the absolute magnitude of the error and not the percentage error is the important factor. For this reason these ΔF^0_{298} values may be considered quite satisfactory.

Before passing, it should be noted that in the case of methane (16b) additional ΔF^0_{298} values of $-12{,}240$ and $-12{,}060$ cal. have been obtained by downward extrapolation of high temperature equilibrium studies on the two reactions.

$$C(\text{graphite}) + 2H_2(g) \rightleftharpoons CH_4(g)$$

and

$$CO_2(g) + 4H_2(g) \rightleftharpoons 2H_2O(g) + CH_4(g)$$

To facilitate comparisons for these several hydrocarbons in the liquid state and to aid in the preparation of figure 1, values of ΔF^0_{298} for liquid methane, ethane, propane, and *n*-butane have been estimated on the assumption of fugacities for these compounds at 25°C. of 160, 21.5, 9.0, and 2.90 atm., respectively. These free energies become, in turn, -9300, -6440, -4940, and -3950 cal. Of course, as the critical temperature of methane is below 298°K., the value in this case is purely hypothetical. Conversely, by utilization of the vapor pressure data in the International Critical Tables (8), hypothetical ΔF^0_{298} values of -2570, $+190$, and $+1520$ cal. have been computed for gaseous *n*-pentane, *n*-heptane, and *n*-octane, respectively.

Effect of a CH_2 *increment*

All these hydrocarbon free energies have been represented graphically in figure 1, where the heavy dots and solid line refer to data for the liquid state and the circles and broken line to data for the compounds as gases. From the plot it is evident that the free energies of the paraffins rise appreciably with increasing length of the hydrocarbon chain and that beginning in the neighborhood of propane the relationships are practically linear. The straight line for the liquid state corresponds to an increase in ΔF^0_{298} of 860 cal. per CH_2 increment; that for the gaseous state to an increase of 1440 cal. per CH_2 increment.

That increment values of this order actually exist can be demonstrated in another way. Rossini (19) has found for the normal paraffin series that above *n*-butane the heat of combustion in the gaseous state increases regularly by 157,000 (±80) cal. per carbon atom. This means that the ΔH^0_{298} of formation must decrease (algebraically) by 5550 cal. per CH_2 group. On the other hand, Parks and Huffman (16d) from their study of entropy regularities among organic compounds have deduced 10.0 (±0.5) E. U. for the increase in entropy in the gaseous state per CH_2 group. Correspondingly the $T\Delta S$ term in equation 2 decreases by about 6740 cal. and consequently ΔF^0_{298} should increase by approximately 1200 cal. If a similar calculation is carried out for the liquid state where the changes in heat of combustion and molal entropy are, respectively, 156,000 (±200) cal. and 7.7 (±0.2) E.U. per carbon atom, the resulting change in ΔF^0_{298} comes out about 870 cal.

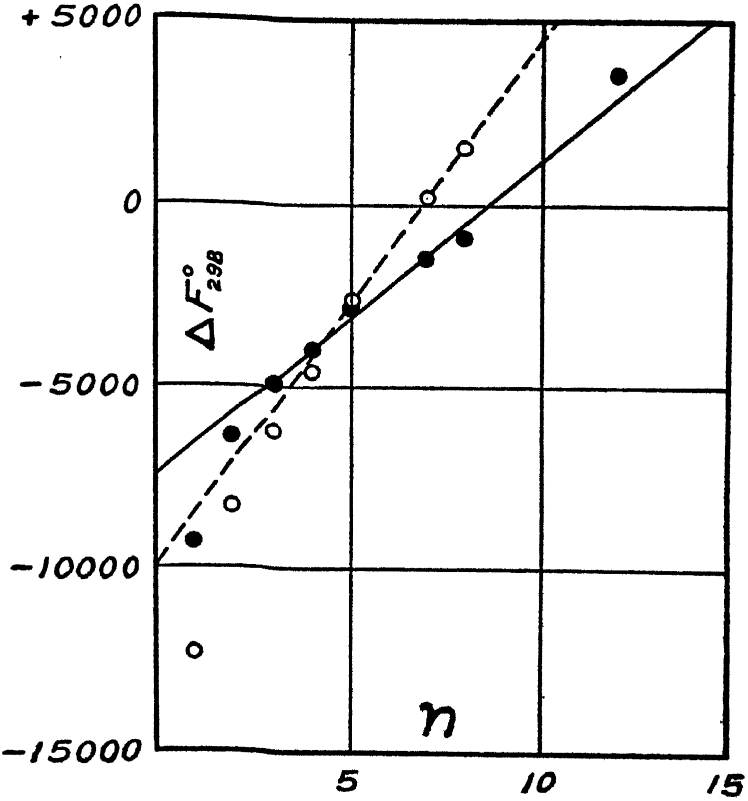

FIG. 1. A plot of the molal free energies of some normal paraffin hydrocarbons against n, the number of carbon atoms in the molecule. The heavy dots and solid line refer to the liquid state; the circles and broken line to the gaseous state.

Effect of branching

Among a group of paraffin isomers the molal free energy generally appears to increase slightly with increased branching in the formula of the hydrocarbon, i.e., the branched isomers become progressively less stable in a thermodynamic sense as compared with the normal compound.

At present the only reasonably satisfactory data available in this field pertain to two groups,—one of seven heptanes (*n*-heptane, 2-methylhexane, 3-ethylpentane, 2,2-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, and 2,2,3-trimethylbutane) and another of three octanes (*n*-octane, 2,2,4-trimethylpentane, and hexamethylethane). Here the U. S. Bureau of Standards (11) in 1928 made the necessary determinations of the heats of combustion and Parks, Huffman, and Thomas (16b) determined the molal entropies with portions of the same materials. Accordingly the resulting free energies should be on a truly comparable basis. The increases in the molal ΔF^0_{298} values for the liquid state over that of the corresponding normal paraffins are given in table 2 in terms of the number of methyl (or ethyl) branches attached on the main chain of the hydrocarbon. While these increases are small and in some cases are not larger than the possible errors in the combustion values, they point in the same direction and yield on the average an effect of +750 cal. per branch.

TABLE 2

Free energy effects of branching (in calories per mole)

	NUMBER OF BRANCHES			
	1	2	3	4
Isomeric heptanes	0 +1200	+1200 +1700 +600	+2200	
Isomeric octanes			+2200	+4500

Average effect of a branch.....................................+750 calories

In one case, that of 2-methylhexane, no increase in ΔF^0_{298} over the value for *n*-heptane was found, and this result was at first considered to be due to a fortuitous error which might mask an effect of only a few hundred calories. However, the equality may be real and it is even possible that certain of the simpler isoparaffins, such as isobutane, may have a slightly lower molal free energy than the normal compound. Thus from his recent value for the heat of combustion of isobutane, Rossini (20) has calculated

$$n\text{-}C_4H_{10} \rightarrow iso\text{-}C_4H_{10};\ \Delta H^0_{298} = -1630\ (\pm 150)\ \text{cal.}$$

From the entropy studies of Parks and Huffman (16d) a prediction of −4 to −5 E.U. for the ΔS^0_{298} of this reaction might now be made. However, even the latter figure would yield, by equation 2, $\Delta F^0_{298} = -140\ (\pm 150)$

cal. for the isomerization process; hence the evidence at present must be considered to favor a slightly greater thermodynamic stability for isobutane than for *n*-butane.

FREE ENERGY VALUES FOR SOME OLEFINS

Thermal data recently obtained make possible the calculation, by equation 2, of accurate free energies for seven olefin hydrocarbons. These ΔF^0_{298} values are given in the last column of table 3, and the essential heat content and entropy data appear in columns 2, 3, and 4. The contributing ΔH^0_{298} values, except in the case of diisobutylene, have been derived by combining the highly accurate heats of hydrogenation for these olefins, measured by Kistiakowsky (12, 13) and his collaborators, with the corresponding ΔH^0_{298} values given in table 1. The ΔH^0_{298} for diisobutylene represents the combination of a heat of hydrogenation of 28,460 (±700) cal., obtained by Mr. B. L. Crawford, Jr. (2), with a ΔH^0_{298} value for 2,2,4-trimethylpentane based on the Bureau of Standards combustion work. The tabulated entropy value for ethylene is a weighted mean of the two values (52.55 and 51.91 E.U.) calculated by statistical methods by Smith

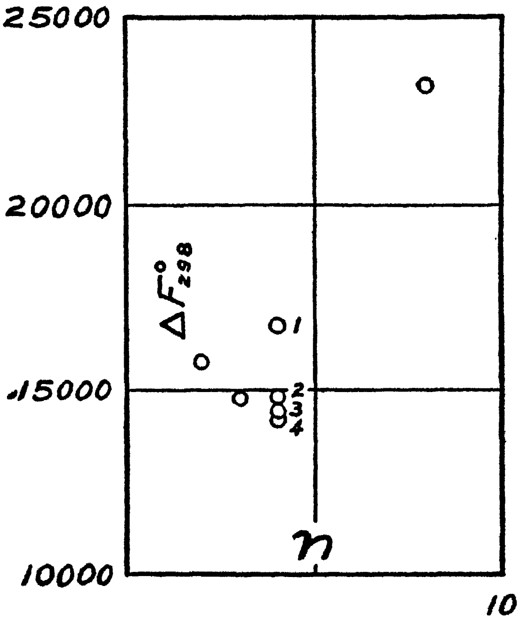

FIG. 2. A plot of the molal free energies of some gaseous olefins against the number of carbon atoms in the molecule. For the butenes the numbers 1, 2, 3, and 4 refer to butene-1, *cis*-butene-2, *trans*-butene-2, and isobutene, respectively.

and Vaughan (21) and by Kassel (10), respectively. The third law values for propylene and diisobutylene are taken from the work of Parks and Huffman (16c); those for the butenes are from a recent investigation of Todd and Parks (22).

These free energy values for the gaseous state are also represented graphically in figure 2. They suffice to delineate fairly well the general free energy relations among the aliphatic olefins, although naturally in view of the great number of possible olefin hydrocarbons and their importance to the chemical industry a larger body of such thermodynamic data is highly desirable. The present values indicate that the effects of increasing the length of the chain and of branching are essentially similar to those among the paraffins if other factors remain unchanged. Thus the free energy increase in going from propylene to butene-1 is within the limits of error the same as that found in going up the paraffin series from propane to *n*-butane. Also, by using the numerical effects derived in the study of the paraffins in conjunction with the tabulated ΔF^0_{298} for *cis*-butene-2, a calculated value of about 22,200 cal. for gaseous diisobutylene is obtainable; this is in fair agreement with the experimental result of 23,150 cal. in table 3.

TABLE 3

Thermodynamic data for some olefins

SUBSTANCE	ΔH^0_{298}	S^0_{298}	ΔS^0_{298}	ΔF^0_{298}
	15°-calories	*E. U.*	*E. U.*	*15°-calories*
Ethylene (g)	11,975	52.3	−12.9	15,820 (±300)
Propylene (g)	4,475	63.1	−34.7	14,820 (±300)
Butene-1 (g)	−480	72.5	−57.9	16,780 (±600)
cis-Butene-2 (g)	−2,250	73.0	−57.4	14,860 (±500)
trans-Butene-2 (g)	−3,200	71.2	−59.2	14,450 (±500)
Isobutene (g)	−4,060	69.0	−61.4	14,240 (±500)
Diisobutylene (l)	−34,890	71.4	−189.3	21,550 (±1500)
Diisobutylene (g)				23,150 (±1500)

Undoubtedly the position of the double bond and geometrical isomerism are other very important factors in determining the magnitude of ΔF^0_{298}. These influences are quite evident in the data for the isomeric butenes, where the order of increasing thermodynamic stability is: butene-1, *cis*-butene-2, *trans*-butene-2, and isobutene. In this connection it should also be noted that merely the addition of one methyl group to the ethylene molecule to yield propylene causes a lowering in molal free energy of 1000 cal., although we have previously seen in the paraffin series that the normal effect of a CH_2 increment is an increase of about 1400 cal. Thus the addition of one or more radicals, such as methyl groups, to the carbon atoms adjacent to the double bond exerts a progressively protective action on the double bond and by a sort of spatial screening tends to render the olefin more like a paraffin hydrocarbon. As yet, however, the available data are too meager for a quantitative evaluation of this screening effect on the molal free energy.

FREE ENERGY DIFFERENCES BETWEEN OLEFINS AND PARAFFINS

The differences in ΔF^0_{298} between the olefins and the corresponding paraffins, with the exception of the ethylene–ethane combination, are approximately 20,000 cal. These differences really represent ΔF^0_{298} for the dehydrogenation reaction

TABLE 4

ΔF^0_{298} *for dehydrogenation reactions*

SUBSTANCE FORMED	BY EQUATION 2	FROM EQUILIBRIUM MEASUREMENTS
Ethylene	24,080	23,330
Propylene	21,040	20,540
Butene-1	21,360	20,710
cis-Butene-2	19,440	19,620
trans-Butene-2	19,030	18,850
Isobutene		18,730
Diisobutylene	20,350	

$$\textit{paraffin hydrocarbon} \rightarrow \textit{olefin hydrocarbon} + H_2$$

and may be readily evaluated in six cases from the free energy values in the preceding tables. The values so obtained have been incorporated in table 4 under the heading "By equation 2."

The dehydrogenation equilibria for ethane have been studied experimentally by Pease and Durgan (17) from 600° to 700°C. and by Frey and Huppke (3) between 400° and 500°C. Their results have been discussed recently in an interesting theoretical paper by Smith and Vaughan (21). The dehydrogenation equilibria for propane, for isobutane, and for *n*-butane to yield a mixture of butene-1, *cis*-butene-2, and *trans*-butene-2 have also been measured experimentally by Frey and Huppke at temperatures of 350°, 400° and 450°C. While the free energy changes for these dehydrogenation processes at the various temperatures are readily obtainable by equation 1, the extrapolation downward to 25°C. provides some uncertainty. The author, however, has attempted this extrapolation on the assumption that ΔC_p for the dehydrogenation is uniformly 4.0 cal. and constant with changing temperature. Tables 3 and 1 provided the necessary data for obtaining the ΔH of the several reactions. In this manner the values of ΔF^0_{298} "from equilibrium measurements" in table 4 were arrived at. While they are undoubtedly more uncertain than the corresponding values by equation 2, there is only an average discrepancy of 2 per cent in the five cases where parallel data exist.

SUMMARY

The conclusions of this review may be briefly summarized as follows:

1. Among the paraffin hydrocarbons the free energy increases with increasing length of chain in the series of normal compounds and in a group of isomers with increased branching.

2. Among the olefin hydrocarbons the effects of increasing the length of the chain and of branching are roughly similar to those among the paraffins, but the position of the double bond and geometrical isomerism are also important factors.

3. The free energy level of the olefins averages about 20,000 cal. above that of the corresponding paraffins.

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THE DETERMINATION OF ACTIVITY COEFFICIENTS FROM THE POTENTIALS OF CONCENTRATION CELLS WITH TRANSFERENCE

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The usefulness of Lewis' conceptions of "activity" and "activity coefficients" in the theory of solutions is now generally conceded. As is well known, activities replace concentrations in thermodynamic equations involving the law of mass action if the components are not perfect solutes. Also the variation of an activity coefficient of a component of a solution from unity is a convenient measure of the departure of that component from the behavior of a perfect solute. A very considerable progress was made when these empirical functions were expressed, by Debye and Hückel, in terms of the electrical state of the solution. According to their theory the variation, from unity, of the activity coefficients of the ion constituents of electrolytes is due to attractions and repulsions of oppositely and like charged particles. Charged particles will tend to arrange themselves, if undisturbed, in regular geometrical order, giving a "lattice structure." Such an arrangement will, however, be continuously disordered by the thermal vibration of the particles. The result of these two opposing effects is that the Gibbs free energies of the ion constituents will be smaller than if the ions were uncharged, and the activity coefficients will, accordingly, be less than unity. Although there remains little doubt that the fundamental assumptions of Debye and Hückel are correct, there is a comparatively small amount of experimental data suitable for testing the theory, particularly in the region of low ion concentrations where their equations are expected to be valid. In dilute solutions complicating secondary effects, not considered in the theory, are most likely to be absent.

Of the various methods available for obtaining activity coefficients, the one depending upon the determination of the potentials of concentration cells is, when applicable, the most convenient and accurate. In contrast to freezing points or boiling points, the measurements are isothermal, and can be carried out at any temperature at which the existence of the cell is physically possible. The concentration cell procedure is superior to these and the vapor pressure method, in that the precision of the measurements does not decrease rapidly as the concentrations of the solutions are lowered. There is, however, a distinct limitation to the electromotive force method, in that reversible electrodes are necessary for the ion constituents of the solute electrolyte. Thus, for sodium chloride solutions, a concentration cell without liquid junction, of which the following is a typical example

$$\text{Ag; AgCl, NaCl}(C_1)\text{; NaHg}_x - \text{NaHg}_x\text{; NaCl}(C_2)\text{, AgCl; Ag} \qquad \text{(Cell A)}$$

involves electrodes reversible to the chloride and sodium ion constituents, in this case silver–silver chloride and sodium amalgam electrodes. Amalgam electrodes, however, require elaborate experimental technique and are limited in the concentration range in which they can be used.

Although it is rarely possible to find electrodes for both ions of a binary electrolyte which are reversible and at the same time convenient to work with experimentally, suitable electrodes for one of the ion constituents are much more frequently available. With such electrodes, concentration cells with liquid junctions can be set up. A cell of this type is the following

$$\text{Ag; AgCl, NaCl}(C_1) : \text{NaCl}(C_2)\text{, AgCl; Ag} \qquad \text{(Cell B)}$$

Another cell of this kind is

$$\text{Ag; AgNO}_3(C_1) : \text{AgNO}_3(C_2)\text{; Ag} \qquad \text{(Cell C)}$$

For silver nitrate as solute a concentration cell without liquid junction is impossible, since no electrode reversible to the nitrate ion is available. The experimental work so far carried out has been on cells B and C at 25°C.

If the transference number t is constant in the concentration range C_1 to C_2 the activity ratio can be computed from the equation:

$$E = -\frac{2tRT}{F}\log\frac{a_1}{a_2} \qquad (1)$$

in which E is the potential of a cell of the type represented by B and C, and a_1 and a_2 are the mean ion activities at the concentrations C_1 and C_2. In general, however, the transference number is a function of the concentration, in which case equation 1 must be replaced by

$$E = -\frac{2RT}{F}\int_{\text{I}}^{\text{II}} t\,\mathrm{d}\log a \qquad (2)$$

the integration being from solution I to solution II.

The validity of equation 2 will be evident from the following considerations. If the cell

$$\text{Ag; AgCl, NaCl}(\mu) : \text{NaCl}(\mu + \mathrm{d}\mu)\text{, AgCl; Ag} \qquad \text{(Cell D)}$$

is set up its potential dE is

$$-F\,dE = t_{Na}d\mu$$

Here NaCl (μ) represents a solution of sodium chloride, the chemical potential of the solute of which is μ, and t_{Na} is the number of equivalents per faraday transferred from the higher to the lower concentration during the reversible operation of the cell. It will be noted that the operation of cell D is, differentially and reversibly, the opposite of the usual process for determining the Hittorf transference number t_{Na}. If now a second cell is made as follows

$$\text{Ag; AgCl, NaCl}(\mu + d\mu) : \text{NaCl}(\mu + d\mu + d\mu'), \text{AgCl; Ag} \qquad \text{(Cell E)}$$

its potential dE' can be obtained from

$$-FdE' = t'_{Na}d\mu'$$

in which t'_{Na} may have a slightly different value from t_{Na}. If cells D and E are put in series the potentials of the electrodes in contact with solutions of like chemical potential will cancel, and the resulting cell will have the same potential as one having the composition

$$\text{Ag, AgCl, NaCl}(\mu), \text{NaCl}(\mu + d\mu + d\mu'), \text{AgCl, Ag} \qquad \text{(Cell F)}$$

Such a series of cells could, of course, be continued indefinitely, from which it follows that

$$\sum - dE = \int - dE = -\frac{1}{F}\int t_{Na}\,d\mu = \frac{2RT}{F}\int t_{Na}\,d\log a$$

the last term following from the conventional definition of mean ion activity.

Although equation 2, or the differential form of it, has been used to obtain transference numbers from E.M.F. data by MacInnes and Beattie, Jones and Dole, Jones and Bradshaw (4, 5, 8), and others, it does not appear to have been used for the purpose of obtaining activity coefficients from E.M.F. and transference data. This is undoubtedly due to the fact that determinations of transference numbers of adequate accuracy have not been available. The recent development, mainly in this laboratory, of the moving boundary method has, however, placed at our disposal transference numbers of high precision, measured over a range of concentrations (7, 10). Furthermore, it has been shown that transference numbers obtained by the moving boundary method agree with the more recent results obtained by the Hittorf method (9).

Values of the transference number of the chloride ion in sodium chloride at concentrations so low that direct measurement is inconvenient or impossible can be obtained by interpolating between the measured values and a limiting value at infinite dilution obtained with the aid of Kohlrausch's law of independent ion mobilities. Using a method of extrapolation, the details of which are given elsewhere (11), which is in accord with the assumption that the Onsager (12) equation is valid for very dilute solutions of electrolytes, the same value for the limiting conductance of the chloride ion, $\Lambda_{0\mathrm{Cl}}$, was obtained from conductance and transference data on solutions of four chlorides. The limiting value of the transference number, $t_{0\mathrm{Cl}}$, is, of course, given by the ratio $t_{0\mathrm{Cl}} = \Lambda_{0\mathrm{Cl}}/\Lambda_{0\mathrm{MCl}}$ in which $\Lambda_{0\mathrm{MCl}}$ is the limiting conductance of the salt MCl. In addition Longsworth (6) has developed an equation, connecting the observed transference number with the concentration, which is useful for interpolation and which gives an extrapolation to infinite dilution in accord with the same assumptions. For the transference number of the nitrate ion in silver nitrate solutions the limiting value was obtained from Kohlrausch's law, and a simple linear equation was found to hold for this and all the measured values.

It should be recalled that the potential of a cell containing a liquid junction of the type

$$\mathrm{NaCl}(C_1) : \mathrm{NaCl}(C_2)$$

where two solutions of the same electrolyte but at different concentrations meet at the boundary, is independent of the manner in which the junction is made, and has a definite constant value. This has been tested by Scatchard and Buehrer (13), who, as a matter of fact, found a very small change of potential (of the order of 0.03 mv.) when a flowing junction between 7.3 and 0.1 *N* hydrochloric acid was allowed to become diffuse by stopping the flow. This slight effect they attribute to temperature gradients in the flowing boundary due to dilution caused by the relatively rapid diffusion. The potentials of the stationary boundaries were found to be constant within the small experimental error.

EXPERIMENTAL

For the determination of the potentials of concentration cells with liquid junction involving silver nitrate as solute (type C), the vessels shown in figure 1 were used. The more dilute solution filled the half-cell B and the more concentrated the half-cell A. The electrodes e and e′ were formed from platinum wires plated with silver. The wires were sealed through narrow tubing, leaving about 1 cm. exposed. Electrical contact was made with mercury. Comparisons of the electrodes in the same silver nitrate solution showed variations of about ±0.02 mv. The data given in table 1 were obtained in this laboratory by Dr. Philip G. Colin. Each reading for an electromotive force is the average of nine readings, using the various possible combinations of electrodes in the two half-cells. After making the liquid junction by bringing the two solutions into contact, the cell reached its final potential immediately and held it with variations of the order of ±0.01 mv. for three hours or longer. The results are additive within the same limit of accuracy. Thus the potential of the combination 0.01 *N*–0.002 *N* is 42.56 mv., whereas the sum of the potentials for the

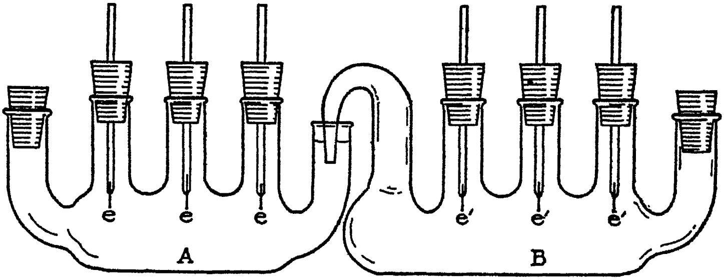

FIG. 1

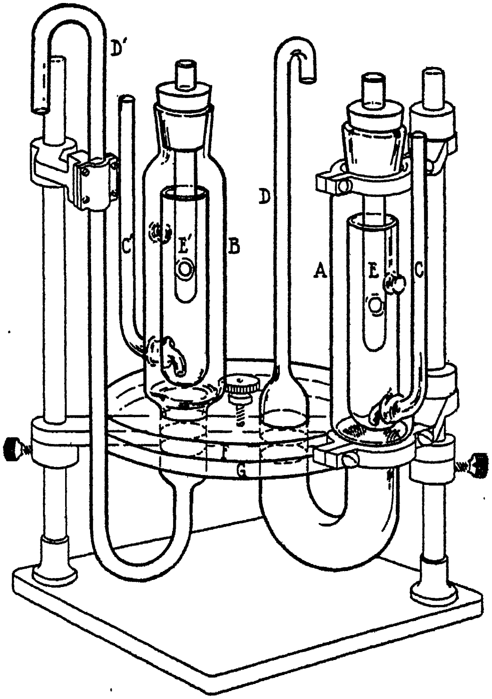

FIG. 2

combinations 0.01 N–0.005 N and 0.005 N–0.002 N is 42.55 mv. Measurements on cells of type C have been made by earlier workers. Their results are, however, very scattered and inaccurate.

A considerable advance in experimental technique was made for the measurement of the concentration cells with liquid junction involving sodium chloride as solute (cells of type B). Since the improved technique has been described in a recent article (1) it will be merely outlined in this place. The apparatus used is shown in figure 2, in position for filling with the solutions. This filling is carried out without bringing the solutions into contact with air, through the tubes C and C′. Contact between the two solutions is produced by rotating the disk F, in a counter-clockwise direction, over the disk G. The potentials are then measured between the electrodes E and E′. For the methods for avoiding contaminations that would affect the results, and for correcting for the unavoidable small amounts of such contaminations, the reader is referred to the original article. Dr. Theodore Shedlovsky has devised a much simpler type of cell which will replace that shown in figure 2 in our future work, which will include measurements on most of the commoner electrolytes. A confirmatory series of determinations of the potential of the silver nitrate concentration cells will shortly be made, using the modified technique.

THE COMPUTATION OF THE ACTIVITY COEFFICIENTS

To compute activity coefficient ratios from cells with transference, it is necessary to perform the indicated integration of equation 2 which may be written in the form:

$$E = -\frac{2RT}{F}\int_{\mathrm{I}}^{\mathrm{II}} t\,(\mathrm{d}\log C + \mathrm{d}\log f) \tag{3}$$

in which C is the salt concentration, f the mean activity coefficient, and t the transference number of the ion to which the electrodes are *not* reversible. This integration has been carried out (*a*) by introducing E and t as empirical functions of C, and (*b*) by a method which is partly graphical. Method *a* cannot conveniently be used unless the empirical equations are relatively simple. For the case of cells involving silver nitrate, simple equations represent the data with accuracy, so that the method can be used as well as method *b*, which is general. The empirical equations for the sodium chloride data are unwieldy, so that method *b* only is available.

Method a. The potentials of the silver nitrate concentration cells, given in table 1, may be expressed with an accuracy of ±0.02 mv. by an equation of the form

$$E = 2t_0\frac{RT}{F}\log C + AC^n + K \tag{4}$$

with the following numerical coefficients

$$0.001E = 0.063373 \log C + 0.02374C^{0.42} + 0.17279 \qquad (5)$$

In these equations t_0 is the limiting value of the transference number of the nitrate ion, and E is the "summed up" potential for the concentration 0.002 N to C. Thus E corresponding to 0.1 N consists of the sum of the potentials for the cells containing the solutions 0.002 N to 0.01 N and 0.01 N to 0.1 N. The measured values of E and the corresponding values from equation 5 are given in the second and third columns of table 2.

TABLE 1

The potentials of silver nitrate concentration cells at 25°C.

C_1	C_2	E.M.F.
moles per liter	*moles per liter*	*mv.*
0.10	0.05	16.78
0.05	0.01	41.03
0.05	0.02	23.04
0.02	0.01	17.99
0.01	0.005	18.15
0.01	0.002	42.56
0.005	0.002	24.40

TABLE 2

Computations of the activity coefficients of silver nitrate in aqueous solution at 25°C.

C	$E_{\text{obsd.}}$	$E_{\text{calcd.}}$	f/f_0 BY METHOD a	$f/f_{0.1}$ BY METHOD b	$f_{\text{obsd.}(a)}$	$f_{\text{obsd.}(b)}$	$f_{\text{calcd.}}$ EXTENDED THEORY
moles per liter	*mv.*	*mv.*					
0.002	0.00	0.00	0.939	1.295_2	0.949	0.950	0.950
0.005	24.40	24.40	0.911	1.257_7	0.922	0.922	0.922
0.01	42.56	42.61	0.883	1.216_6	0.894	0.892	0.894
0.02	60.55	60.53	0.848	1.170_3	0.857	0.858	0.857
0.05	83.59	83.59	0.785	1.083_4	0.794	0.795	0.794
0.10	100.37	100.39	0.725	1.000_0	0.734	0.733	0.735

The transference number of the nitrate ion in silver nitrate can be expressed by the empirical equation

$$t \quad t_0 - bC \qquad (6)$$

$$t = 0.5357 - 0.039C \qquad (7)$$

as is shown in table 3, in which the measured transference numbers obtained in this laboratory by Dr. Irving A. Cowperthwaite are given in the second column and the values from equation 7 are given in the third column.

With the use of equations 4 and 6, equation 3 can be put in the form

$$\frac{\mathrm{d}E}{t} = 2R' \,\mathrm{d} \log Cf = \frac{2t_0R' \,\mathrm{d}C}{2.303(t_0 - bC)C} - \frac{nAC^{n-1}}{(t_0 - bC)} \,\mathrm{d}C \tag{8}$$

where R' replaces RT/F. After expanding the second term on the right-hand side, integrating between the limits C and zero, introducing the numerical coefficients from equations 5 and 7 and solving for $\log f/f_0$, we have the equation

$$\begin{aligned} -\log f/f_0 = \log\,(1 - 0.07280C) + 0.3746(C^{0.42} + 0.021533C^{1.42} \\ + 0.0008733C^{2.42}) \end{aligned} \tag{9}$$

Equation 9 cannot be used for extrapolation, since equation 5 is valid only over the concentration range investigated. Log f_0 is an integration constant which would be zero if the equation held to $C = 0$. The ratios f/f_0 for silver nitrate, given in the fourth column of table 2, were obtained from equation 9.

TABLE 3

Transference numbers for the nitrate ion in silver nitrate solutions

C	$t_{\mathrm{obsd.}}$	$t_{\mathrm{calcd.}}$
moles per liter		
0.10	0.5318	0.5318
0.05	0.5336	0.5337
0.02	0.5348	0.5349
0.01	0.5352	0.5353
0.00	[0.5357]	0.5357

Method b. For our data on sodium chloride concentration cells and transference numbers, given in the first three columns of table 4 (1), the following more general method devised by Dr. L. G. Longsworth for computing the activity coefficients was used. The transference number, t_{Na}, at any concentration may be expressed by

$$t_{Na} = t_1 + \Delta t$$

t_1 being the value at some reference concentration, in this case 0.1 N. If the potentials are stated in millivolts at 25°C. equation 3 becomes

$$\mathrm{d}E = -2 \times 59.144(t_1 + \Delta t)(\mathrm{d} \log C + \mathrm{d} \log f) \tag{10}$$

Expanding and rearranging we obtain

$$-\mathrm{d}E/118.29\, t_1 = \mathrm{d} \log C + \Delta t/t_1 \cdot \mathrm{d} \log C + \mathrm{d} \log f + \Delta t/t_1 \cdot \mathrm{d} \log f \tag{11}$$

Integrating and again rearranging yields

$$\Delta \log f = \log f_2 - \log f_1 = \frac{-E}{118.29 t_1} - (\log C_2 - \log C_1)$$
$$- \frac{1}{t_1} \int_{\mathrm{I}}^{\mathrm{II}} \Delta t \, \mathrm{d} \log C - \frac{1}{t_1} \int_{\mathrm{I}}^{\mathrm{II}} \Delta t \, \mathrm{d} \, \Delta \log f \qquad (12)$$

Of the four terms on the right-hand side of this equation, the first two are computed directly from the data. The third term is obtained by graphical integration, using a plot of Δt values against values of $\log C$. The fourth term, of relatively small magnitude, is obtained by graphical integration, using preliminary values of $\Delta \log f$, obtained by adding the first three terms of the equation, and plotting against Δt. This process could be repeated with more accurate values of $\Delta \log f$, but a further approximation was not found to be necessary. The resulting values of $\Delta \log f$ for sodium chloride are given in the fourth column of table 4.

TABLE 4

The activity coefficients of sodium chloride at 25°C.

NORMALITY C	E.M.F. IN MV.	TRANSFERENCE NO. t_{Na}	LOG ACTIVITY COEFFICIENT RATIO, $\Delta \log f$	ACTIVITY COEFFICIENTS		
				f (obsd.)	f (computed from equation 13)	f (computed from equation 17)
0.004984_9	-56.45_0	0.3930	−0.0758	0.9283	0.9281	0.9281
0.006978_6	-49.90_7	0.3925	−0.0705	0.9171	0.9171	0.9169
0.009967_0	-43.02_9	0.3918	−0.0640	0.9034	0.9036	0.9034
0.019934_4	-29.80_4	0.3902	−0.0489	0.8726	0.8726	0.8724
0.02989_7	-22.18_1	0.3891	−0.0382	0.8513	0.8515	0.8515
0.03985_5	-16.81_8	0.3883	−0.0300	0.8354	0.8354	0.8354
0.04981_0	-12.69_5	0.3876	−0.0230	0.8221	0.8221	0.8224
0.05976_2	-9.31_7	0.3870	−0.0176	0.8119	0.8110	0.8115
0.07965_5	-4.05_6	0.3861	−0.0079	0.7940	0.7925	0.7938
0.09953_3	0	0.3855	0	(0.7796)	0.7779	0.7796

In the fifth column of table 2 values of $f/f_{0.1}$ (i.e., the antilogs of $\Delta \log f$) are given. These were obtained by method *b* from the data on silver nitrate.

THE INTERPRETATION OF THE ACTIVITY COEFFICIENT RATIOS

To provide a basis for the activity coefficients, f, such that they will approach unity as the concentration is progressively decreased, use can be made of the familiar equation of the Debye-Hückel theory

$$- \log f = \alpha \sqrt{C} / (1 + \beta \sqrt{C}) \qquad (13)$$

in which α depends upon the temperature, the dielectric constant, and universal constants, and β depends upon these factors, and, in addition, upon the distances of closest approach of the ions. This equation is valid for dilute solutions containing relatively large ions. To use this equation 13 with the data in table 4 the following procedure was found to be convenient. We may set

$$\log f = A - \Delta \log f \tag{14}$$

in which A is a constant. Combining equations 13 and 14 and rearranging terms

$$\Delta \log f - \alpha\sqrt{C} = A + \beta(A - \Delta \log f)\sqrt{C} \tag{15}$$

Thus, through the range of validity of equation 13 a plot of $\Delta \log f - \alpha\sqrt{C}$ against $(A - \Delta \log f)\sqrt{C}$ should be a straight line with intercept A and slope β. The constant A is obtained by means of a short series of approximations. Using a value of $\alpha = 0.5056$ at 25°C., this computation yields a value of A of -0.1081 and of β of 1.463. This value of β corresponds to a distance of closest approach of 4.45 Å., which is sufficiently large for the higher terms of the extended theory of Gronwall, La Mer, and Sandved (2) to be negligible.

In columns 5 and 6 of table 4 are given the observed activity coefficients and those computed from equation 13. It will be observed that the agreement of the corresponding values is excellent up to a concentration of 0.04 or 0.05, above which there is a progressive deviation. For solutions of higher concentrations Hückel (3) has proposed an equation of the form

$$\log f = -\frac{\alpha\sqrt{C}}{1 + \beta\sqrt{C}} + DC \tag{16}$$

in which D is an additional constant. Using this extra term, agreement between observed and computed values of the activity coefficient is obtained as high as the measurements were made, which was up to 0.1 molar. This can be seen by comparing the values of columns 5 and 7 of table 4. The differences in the observed and computed values are of the order of 0.0002. The more complete equation connecting the activity coefficient and the concentration is

$$\log f = -\frac{0.5056\sqrt{C}}{1 + 1.315\sqrt{C}} + 0.047\,C \tag{17}$$

However, as can be seen, to attain this agreement between the observed and computed values of the activity coefficient it was necessary to change the value of β from 1.463 to 1.315. Equally good agreement between observed and computed activity coefficients may be obtained with a range of values of the constants β and D, a decrease in one of them compensating for an increase of the other. It is evident that the Hückel equation is useful for expressing the data, at least in this case, although it is in large measure empirical. The activity coefficients for sodium chloride and their relation to the limiting law

$$-\log f = \alpha\sqrt{C}$$

are shown in figure 3, where the values of log f are plotted as ordinates against the square root of the concentration as abscissas.

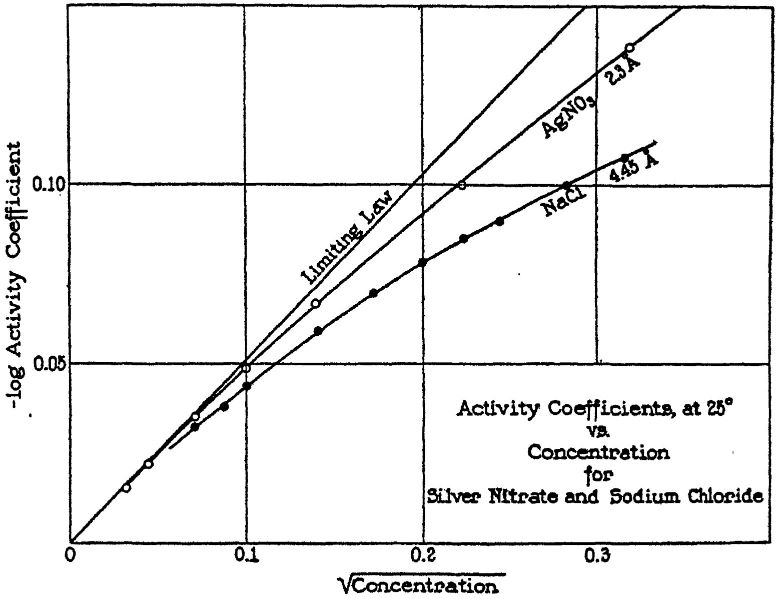

FIG. 3

For the data on silver nitrate equation 13 will express the data with a distance of closest approach of 2.0 Å. However, if that parameter is as small as this preliminary value would indicate, the computations should be made with the more complete theory in the form given it by Gronwall, La Mer, and Sandved (2), who have extended it to include higher terms omitted in the mathematical development in its earlier form. For the details of the calculation the reader is referred to the original article. With the aid of that theory a value of f_0 or $f_{0.1}$ necessary for converting the activity ratios, obtained by methods a and b, respectively, was obtained. The resulting activity coefficients are given in columns 6 and 7 of table 2. It will be observed that the two methods of computation yield practically the same results. Column 8 contains the activity coefficients calculated directly from the extended theory, using a distance of closest approach of 2.3 Å. The agreement between the observed and computed values is excellent. The activity coefficients for silver nitrate are also plotted in figure 3.

SUMMARY

Using a method involving the determination of the potentials of concentration cells with liquid junctions, and of transference numbers, accurate values of the activity coefficients of sodium chloride and of silver nitrate in aqueous solution at 25°C. have been determined. The method requires a type of electrode reversible to only one of the constituents of a binary electrolyte, and thus greatly extends the range of electrolytes for which the concentration cell method is available for obtaining the thermodynamic properties of the substances in solution.

The data on the activity coefficients for sodium chloride follow the Debye-Hückel relations in their original form up to a concentration of 0.05 normal, with a distance of closest approach of 4.45 Å. For the activity coefficients of silver nitrate, however, the extended theory of Gronwall, La Mer, and Sandved should be used. The extended theory accurately expresses the data for that substance if the distance of closest approach of 2.3 Å. is used.

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DISCUSSION

DR. HILDEBRAND: There used to be a great deal of discussion about different methods of setting up a liquid–liquid junction; will you tell us the present answer to the question?

DR. MACINNES: I can give a decisive answer only for the type of junction involved in the cells of the kind discussed in our paper. These, it will be recalled, are of the form:

$$\mathrm{NaCl}(C_1) : \mathrm{NaCl}(C_2) \qquad \text{(Cell A)}$$

in which two solutions *of the same electrolyte* meet at the boundary. It has been found by repeated and careful experiments that potentials of cells involving such liquid junctions are quite independent of the way they are made. There are two qualifications to this statement. One is that the mixed solutions must not reach the electrodes. The other is that large heat effects due to mixing of the solutions at the junction must not occur. We have found that a junction, initially sharp, can be stirred without changing the cell potential. Also we have found that the potential of the cell:

$$\mathrm{Ag; AgCl, NaCl}\ (0.1\ M) : \mathrm{NaCl}\ (0.04\ M), \mathrm{AgCl; Ag} \qquad \text{(Cell B)}$$

was equal within 0.001 mv. to the cell:

$$\mathrm{Ag; AgCl, NaCl}\ (0.1\ M) : \mathrm{NaCl}\ (0.2\ M) : \mathrm{NaCl}\ (0.04\ M), \mathrm{AgCl; Ag} \qquad \text{(Cell C)}$$

Here it is seen that in cell C a strong solution is interposed between the two solutions in cell B, but that all three solutions are of the same electrolyte.

Theoretically this constancy is due to the fact that the transference number t and the activity a in equation 2 are both functions of the concentration C. From the point of view of the liquid junction, all computations of the potentials of such junctions start from the equation (for uni-univalent electrolytes):

$$FE_j = -RT \int \sum_i t_i \, \mathrm{d} \log a_i$$

in which E_j is the liquid junction potential, t_i and a_i are, respectively, the transference number and the (hypothetical) single ion activity of the ion species i. The summation is over all the ion species present and the integration is from values of the variables corresponding to one of the solutions to those in the other. For liquid junctions of type A, t_i and a_i

are single valued functions of the concentration C for all mixtures of the two solutions in contact, and the integration will therefore be independent of the spatial arrangement of these mixtures. This is not true of junctions of the type

$$\text{NaCl : HCl} \qquad \text{(D)}$$

for instance. Here the transference numbers and activities will depend upon the way that the two solutions are brought together. This theoretical deduction is also supported by experiment. The potentials of cells involving junctions of type D are dependent upon whether they are sharp, as with a flowing junction, or whether appreciable diffusion has taken place.

THE ENTROPY OF AQUEOUS IONS AND THE NATURE OF THE ENTROPY OF HYDRATION

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A knowledge of the partial molal entropies of ions in aqueous solutions extends the applications of the third law of thermodynamics to reactions involving electrolytes by means of the equation relating the free energy, ΔF, the reaction heat, ΔH, entropy, ΔS, and the absolute temperature, T:

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

These partial molal entropies are fundamental thermodynamic quantities, and give definite evidence regarding the nature of the forces acting between the ions and the solvent molecules.

The most direct method of obtaining ionic entropies involves a knowledge of the entropy of a salt, and its entropy of solution, the latter quantity being calculated from the free energy and heat of solution by equation 1. The sum of the entropies of the ions in solution is then given as the ΔS of solution plus the entropy of the solid salt. Since it is more convenient to use relative values for the ionic entropies instead of these sums, the entropy of H^+ has been chosen as zero and all values are given in reference to this arbitrary choice. Many examples of this method of obtaining ionic entropies are to be found in table 1. All values are given for the standard state which is chosen, again arbitrarily, as the hypothetical 1 molal solution with the heat content of the ions at infinite dilution.

There are also a good many other reactions involving aqueous ions for which both the heat and free energy are known, as, for example, the solution of potassium in dilute acid and the combination of chlorine and hydrogen to form hydrochloric acid. For some of these, the reaction heats are large and the data are not of great accuracy. However, the best of the available data for these reactions are also summarized in table 1. This table has been taken, unless otherwise noted, from a paper by Latimer, Schutz, and Hicks (6) and this reference should be consulted for the details of these calculations.

The values for the entropies of the substances appearing in table 1 have all been obtained from specific heat measurements, using the third law of

TABLE 1

Summary of entropy calculations

ΔH^0 and ΔF^0 in calories per mole. ΔS^0 in calories per degree per mole. The entropy data for the elements and compounds used in these calculations are summarized in table 2 of ref. 6

REACTION	$\Delta H^0_{298.1}$	$\Delta F^0_{298.1}$	$\Delta S^0_{298.1}$	
				$\bar{S}^0_{\mathrm{Cl}^-}$
$\frac{1}{2}H_2+AgCl(s)=H^++Cl^-+Ag(s)$	−9600	−5125	−15.01	13.49
$HCl(g)=H^++Cl^-$	−17880	−8598	−31.14	13.52
$\frac{1}{2}H_2+\frac{1}{2}Cl_2(g)=H^++Cl^-$	−39940	−31373	−28.75	13.52
	−39940	−31367	−28.77	13.50
				$\bar{S}^0_{\mathrm{Ag}^+}$
$AgCl(s)=Ag^++Cl^-$	15980	13297	9.0	18.5
	15980	13329	8.9	18.4
$Ag+\frac{1}{2}Cl_2(g)=Ag^++Cl^-$	−14330	−12890	−4.8	18.4
$Ag+H^+=Ag^++\frac{1}{2}H_2$	25540	18448	23.8	18.3
				$\bar{S}^0_{\mathrm{Hg_2}^{++}}$
$2Hg(l)+2H^+=Hg_2^{++}+H_2$	40160	36854	11.1	16.5
$Hg_2Cl_2(s)=Hg_2^{++}+2Cl^-$	23740	24446	−2.4	16.2
				$\bar{S}^0_{\mathrm{Br}^-}$
$\frac{1}{2}Br_2+\frac{1}{2}H_2=Br^-+H^+$	−28945	−24577	−14.65	19.3
$AgCl(s)+Br^-=AgBr(s)+Cl^-$	−4457	−3461	−3.3	19.4
$AgBr(s)+\frac{1}{2}H_2=Ag(s)+H^++Br^-$	−5135	−1673	−11.6	19.5
				$\bar{S}^0_{\mathrm{I}^-}$
$AgI(s)=Ag^++I^-$	26710	21889	16.2	25.4
$\frac{1}{2}H_2+\frac{1}{2}I_2=H^++I^-$	−13660	−12361	−4.3	25.2
$HI(g)=H^++I^-$	−19550	−12676	−23.0	26.5
$Ag(s)+\frac{1}{2}I_2(s)=Ag^++I^-$	11870	6087	19.4	24.9
				$\bar{S}^0_{\mathrm{Tl}^+}$
$Tl+H^+=Tl^++\frac{1}{2}H_2$	935	−7760	29.2	28.5
$Tl+\frac{1}{2}Cl_2(g)=Tl^++Cl^-$	−38790	−39105	1.0	29.1
	−38930	−39105	0.6	28.7
$TlCl=Tl^++Cl^-$	10125	5086	16.9	29.2
$Tl+\frac{1}{2}Br_2(l)=Tl^++Br^-$	−27990	−32337	14.5	28.4
$Tl+\frac{1}{2}I_2(l)=Tl^++I^-$	−12720	−20082	24.7	28.0
$TlI=Tl^++I^-$	17530	9938	25.5	28.6
				$\bar{S}^0_{\mathrm{NO_3}^-}$
$TlNO_3=Tl^++NO_3^-$	9970	1790	27.4	36.9
				$\bar{S}^0_{\mathrm{Ba}^{++}}$
$Ba(NO_3)_2=Ba^{++}+2NO_3^-$	10200	3200	23.5	0.8
				$\bar{S}^0_{\mathrm{OH}^-}$
$H_2O=H^++OH^-$	13329	19122	−19.4	−2.5
				$\bar{S}^0_{\mathrm{Ca}^{++}}$
$Ca(OH)_2=Ca^{++}+2OH^-$	−3385	6960	−34.7	−11.4
				$\bar{S}^0_{\mathrm{Mg}^{++}}$
$Mg(OH)_2=Mg^{++}+2OH^-$	−1180	15410	−55.6	−35.5

TABLE 1—*Continued*

REACTION	$\Delta H^0_{298.1}$	$\Delta F^0_{298.1}$	$\Delta S^0_{298.1}$	
				$\bar{S}^0_{K^+}$
$KCl = K^+ + Cl^-$	4119	−1207	17.9	24.3
$KBr = K^+ + Br^-$	4726(2)	−1546	21.0	24.1
$K + H^+ = K^+ + \frac{1}{2}H_2$	−60340	−67431	23.8	24.7
				$\bar{S}^0_{S^{--}}$
$H_2 + S(s) = 2H^+ + S^{=}$	10040	23450	−45.0	−6.2
$H_2S(g) = 2H^+ + S^{=}$	15300	31290	−53.6	−5.4
				$\bar{S}^0_{SO_4^{--}}$
$Ag_2SO_4 = 2Ag^+ + SO_4^{=}$	4210	6722	−8.4	2.8
$BaSO_4 = Ba^{++} + SO_4^{=}$	5455	13718	−27.7	3.0
$CaSO_4\cdot 2H_2O = Ca^{++} + SO_4^{=} + 2H_2O$	270	6308	−20.2	3.8
				$\bar{S}^0_{Na^+}$
$NaCl = Na^+ + Cl^-$	1019	−2524	11.9	15.7
	1019	−2161	10.7	14.4
$NaBr = Na^+ + Br^-$	−44(2)	−4231	14.0	14.7
$Na + H^+ = Na^+ + \frac{1}{2}H_2$	−57520	−62588	17.0	13.9
				$\bar{S}^0_{Pb^{++}}$
$Pb + 2H^+ = Pb^{++} + H_2$	−600	−5877	17.7	2.1
$Pb + Cl_2(g) = Pb^{++} + 2Cl^-$	−80330	−68567	−39.5	2.4
$PbCl_2 = Pb^{++} + 2Cl^-$	5060	6483	−4.8	2.1
				$\bar{S}^0_{Fe^{++}}$
$Fe + Hg_2Cl_2(s) = Fe^{++} + 2Cl^- + 2Hg(l)$	−37500	−32585	−16.5	−28.0
$Fe + 2TlCl(s) = Fe^{++} + 2Cl^- + 2Tl$	−3170	5455	−28.9	−27.6
$Fe + 2H^+ = Fe^{++} + H_2$	−20800	−20240	−1.9	−26.6
				$\bar{S}^0_{Fe^{+++}}$
$Fe^{++} + H^+ = Fe^{+++} + \frac{1}{2}H_2$	11240	17230	−20.1	−63.1
$Fe^{+++} + Ag = Ag^+ + Fe^{++}$	14300	1218	43.9	−63.0
				$\bar{S}^0_{Al^{+++}}$
$CsAl(SO_4)_2\cdot 12H_2O = Cs^+ + Al^{+++} + 2SO_4^{=} + 12H_2O$	13560	12910	2.18	−71.7
				$\bar{S}^0_{Li^+}$
$Li + H^+ = Li^+ + \frac{1}{2}H_2$	−66380	−68248	6.2	−1.8
				$\bar{S}^0_{Rb^+}$
$Rb + H^+ = Rb^+ + \frac{1}{2}H_2$	−61210	−67473	21.0	22.8
				$\bar{S}^0_{Cu^{++}}$
$Cu + 2H^+ = Cu^{++} + H_2$	16640	15912	2.4	−21.0
				$\bar{S}^0_{Cd^{++}}$
$Cd + 2H^+ = Cd^{++} + H_2$	−16510	−18348	6.2	−12.7
				$\bar{S}^0_{Sn^{++}}$
$Sn + 2H^+ = Sn^{++} + H_2$	−2390	−6276	13.0	−5.9
				$\bar{S}^0_{Hg^{++}}$
$Hg + 2H^+ = Hg^{++} + H_2$	41590	39679	6.4	−6.5
				$\bar{S}^0_{Zn^{++}}$
$Zn + 2H^+ = Zn^{++} + H_2$	−36720	−34984	−5.8	−27.2

TABLE 1—*Concluded*

REACTION	$\Delta H^0_{298.1}$	$\Delta F^0_{298.1}$	$\Delta S^0_{298.1}$	
				$\bar{S}^0_{ClO_3^-}$
$KClO_3 = K^+ + ClO_3^-$....................	10120	1277	29.7	39.3
				$\bar{S}^0_{BrO_3^-}$
$Ba(BrO_3)_2 \cdot H_2O = Ba^{++} + 2BrO_3^- + H_2O$..	15360	7170	26.5	38.7
$KBrO_3 = K^+ + BrO_3^-$..................	9540	1690	26.3	37.4
				$\bar{S}^0_{IO_3^-}$
$AgIO_3 = Ag^+ + IO_3^-$....................	13200	10200	10.1	27.7
$KIO_3 = K^+ + IO_3^-$.....................	6340	1770	15.3	26.9
				$\bar{S}^0_{ClO_4^-}$
$KClO_4 = K^+ + ClO_4^-$...................	12115	2690	31.6	43.1
				$\bar{S}^0_{C_2O_4^{--}}$
$CaC_2O_4 \cdot H_2O = Ca^{++} + C_2O_4^{=} + H_2O$......	5090	11790	−22.5	9.3
				$\bar{S}^0_{CO_3^{--}}$
$CaCO_3 + C_2O_4^{=} + H_2O$ $= CaC_2O_4 \cdot H_2O + CO_3^{=}$..............	−7460	−306	−24.0	−13.1
$C + \frac{3}{2}O_2 + H_2 = 2H^+ + CO_3^{=}$..............	−161100	−125760	−118.5	−12.5
$CaCO_3 = Ca^{++} + CO_3^{=}$.................	−2780	10922	−46.0	−12.6
				$\bar{S}^0_{HCO_3^-}$
$CaCO_{3\,calc.} + CO_2 + H_2O = Ca^{++} + 2HCO_3^-$.	−8588(3)	7980(3)	−55.6	23.0
$CaCO_{3\,arag.} + CO_2 + H_2O = Ca^{++} + 2HCO_3^-$.	−8550(3)	7788(3)	−54.8	22.8
				$\bar{S}^0_{Sr^{++}}$
$SrCO_3 + CO_2 + H_2O = Sr^{++} + 2HCO_3^-$....	−6740(3)	9052(3)	−53.0	−7.8

thermodynamics, and it is obvious from the consistency of the data that this method may be applied to salts of non-magnetic ions and their aqueous solutions without serious danger of errors due to zero point entropy or transitions at very low temperatures. It should also be noted that the checks obtained are, for almost every ion, more numerous than the cases listed under that ion. For example, if we use our values for iodide, iodate, ferrous, ferric, and sulfate ions, we can then calculate by five additional methods the entropy of silver ion. The maximum deviation from the mean (which includes also the error in the negative ion) is 0.8 E.U. A summary of values for all the ions which have been determined is given in table 2.

One of the most useful applications of the ionic entropies to thermodynamic problems is the calculation of oxidation–reduction potentials for those elements which are either so highly electropositive or highly electronegative that direct equilibrium measurements are impossible in water solutions. A summary of the calculations for a number of such elements is given in table 3, together with similar calculations for a few examples in which direct comparison may be made with the experimental values.

The agreement in the first three cases indicates the reliance which may be placed in the calculations, but unfortunately the entropy values which have been used to calculate the ΔS terms and also the reaction heats for many of the other reactions are not known with sufficient accuracy to place the same confidence in all of the last six examples. However, these values are certainly to be preferred to any of the attempts to measure these equilibria directly.

TABLE 2

Entropies of aqueous ions at 298.1°

Values are given in calories per degree per mole

IONS	ENTROPIES	IONS	ENTROPIES
Li^+	1.8	Fe^{++}	−27.4±0.7
Na^+	14.7±1.0	Fe^{+++}	−63.0
K^+	24.6±0.5	Al^{+++}	−71.7
Rb^+	22.8	F^-	−5.0
Tl^+	28.6±0.3	Cl^-	13.5±0.1
Hg_2^{++}	16.4±0.5	Br^-	19.4±0.4
Ag^+	18.4±0.2	I^-	25.7±0.7
Mg^{++}	−35.5	NO_3^-	36.9
		ClO_4^-	43.1
Ca^{++}	−11.4	ClO_3^-	39.3
Ba^{++}	0.8	BrO_3^-	37.7±1.0
Cu^{++}	−21.0	IO_3^-	27.1±1.0
Zn^{++}	−27.2	OH^-	−2.5
Cd^{++}	−12.7	CO_3^{--}	−12.7±0.5
Sn^{++}	−5.9	SO_4^{--}	3.5±0.5
Hg^{++}	−6.5	$C_2O_4^{--}$	9.3
Pb^{++}	2.2±0.2	S^{--}	−5.8±1.0
Sn^{++}	−7.8	HCO_3^-	−22.9

TABLE 3

Calculation of oxidation-reduction potentials

REACTION	$\Delta H^0_{298.1}$	$\Delta S^0_{298.1}$	$\Delta F^0_{298.1}$	E^0 CALCD.	E^0 EXPTL.
$Ag + H^+ = Ag^+ + \frac{1}{2}H_2$	25540	24.0	18390	−0.798	−0.799
$Pb + 2H^+ = Pb^{++} + H_2$	−600	17.8	−5910	−0.127	−0.128
$\frac{1}{2}I_2 + \frac{1}{2}H_2 = H^+ + I^-$	−13660	−3.9	−12480	−0.536	−0.539
$Mg + 2H^+ = Mg^{++} + H_2$	−110200	−12.1	−106600	+2.31	
$Ca + 2H^+ = Ca^{++} + H_2$	−129800	+8.8	−132400	+2.86	
$Sr + 2H^+ = Sr^{++} + H_2$	−130200	+11.4	−133600	+2.90	
$Ba + 2H^+ = Ba^{++} + H_2$	−128600	+19.6	−134500	+2.91	
$Al + 3H^+ = Al^{+++} + \frac{3}{2}H_2$	−127000	−31.7	−117500	+1.70	
$Cl^- + \frac{1}{2}F_2 = F^- + \frac{1}{2}Cl_2$	−39900	−16.0	−35100	−1.52	

The measurement of the free energy of solution, i.e., to form the hypothetical 1 molal solution, of very slightly soluble salts or of very highly soluble salts is often a problem of unusual difficulty. A knowledge of the ionic entropies and the entropy of the salts permits the accurate calculation of this free energy from the heat of solution, and, conversely, if the solubility of a salt is known, the heat of solution may be calculated by equation 1. If both the heat of solution and molal solubility are determined experimentally, one may calculate this activity coefficient of the salt in solution, but not many of the heats of solution and entropy values are of sufficient accuracy to justify this procedure at present.

It was pointed out by Latimer and Buffington (4) in their initial paper upon ionic entropies, that the so-called entropy of hydration is a function of the size and charge of the ion.

$$\Delta S_{\text{hydration}} = f\left(\frac{e^2}{r}\right) \tag{2}$$

The hydration entropy is defined as the difference between the partial molal entropy of the ion in solution and the entropy of the ion as a gas which, provided it is all translational entropy, may be calculated by the Sackur equation.

$$S_{298.1} = \frac{3}{2} R \ln M + 26.03 \tag{3}$$

where M is the molecular weight and the constant is for the gas at 1 atmosphere and 298.1°A.

In figure 1 these hydration entropies have been plotted against the ionic radii as given by Pauling (7). The values fall fairly well upon straight lines, showing that specific hydration effects are small in comparison to the electrostatic action of the charge upon the water dipoles. The values for the entropies of the ions in solution are not absolute but are relative to hydrogen equal to zero, so it is not to be expected that the lines for the monovalent positive and negative ions should coincide; however, if the hydration entropies are the same function of the radii, the lines should be parallel. Now theoretical considerations suggest that the effective radius of an ion in solution is the distance from the center of the ion to the center of the water dipole. Since the negative ions have the hydrogens of the water directed in and the positive ions have the hydrogen directed out, the effective radii of the negative ions will be but slightly greater than the crystal radius, while those for the positive ions will be considerably larger. If we choose this increase in the positive ion radii as 0.7 A.U., the curve for the positive ions in figure 1 is shifted to the position of the dotted line, and is approximately parallel to that of the negative ions. The difference between the two lines should now be due to the difference in the relative and absolute entropies of the aqueous ions, and is in fact in close agreement with the recent determination of the absolute partial molal entropy of chloride ion by Eastman and Young (8), who obtain as a provisional value 18.1 ± 0.5 E.U. in comparison to our value relative to $H^+ = 0$ of 13.5 E.U. The difference 4.6 E.U. should then be added, in the case of the monovalent negative ions, and subtracted for the monovalent positive ions, in order to convert the relative entropies to absolute entropies, i.e., the two curves in figure 1 should differ by 9.2 E.U. The agreement is shown in figure 2 in

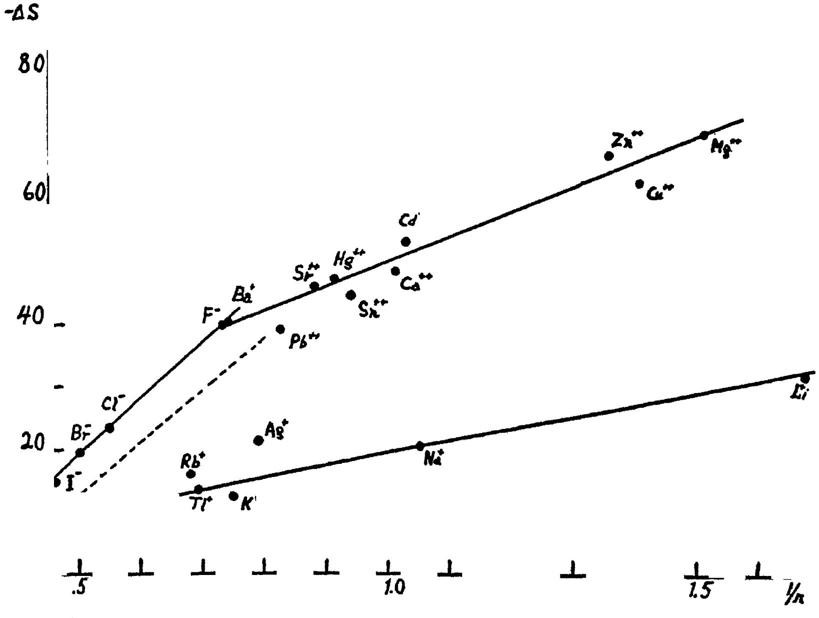

FIG. 1. Relative entropy of hydration against reciprocal ionic radius

which the absolute entropies of hydration have been plotted against the reciprocal of the effective radii as defined above.

Latimer and Kasper (5) were able to show that the entropy of hydration of the larger monovalent ions could be accounted for entirely as the decrease in entropy of the water due to the pressure set up in the polarizable medium by the charge on the ion. The change in entropy with pressure is given by the expression

$$dS = -\left(\frac{dV}{dT}\right)_P dP \qquad (4)$$

For a differential unit of volume the entropy change is obtained by integrating this expression with respect to the pressure and the total entropy change about the ion is then obtained by integrating over the total volume of the water outside the ion cavity.

$$\Delta S = -\int_{r}^{\alpha}\int_{1}^{P}\frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)_P \mathrm{d}P\, 4\pi r^2 \mathrm{d}r \tag{5}$$

For the pressure they used the expression

$$P = \frac{(3+2D)(D-1)}{40D^2}\,\frac{e^2}{r^4} = 375{,}000\,\frac{e}{r^4}\text{ kg. per cm.}^2 \tag{6}$$

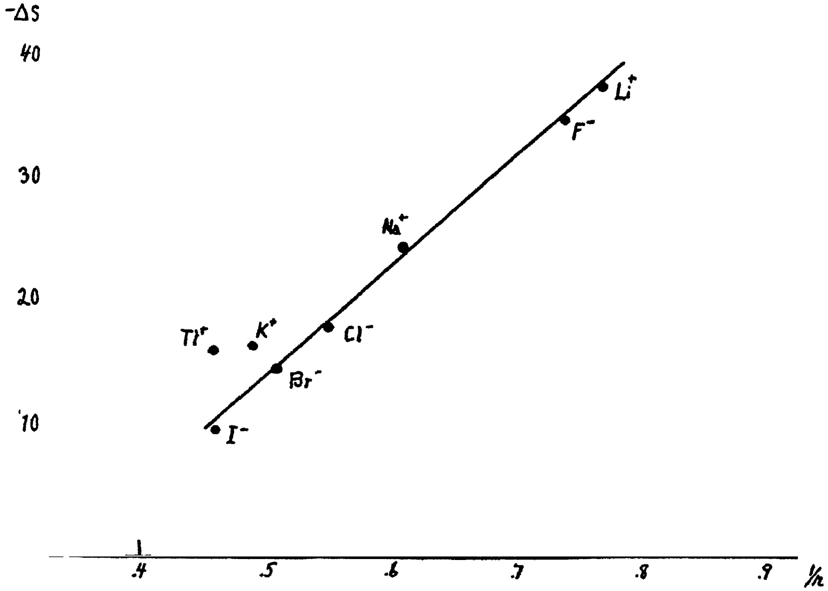

FIG. 2. Absolute entropy of hydration against effective ionic radius

where e is the charge in faradays, r is expressed in Ångström units, and the constant is for water at 25°C. The deviation of the actual pressure at very high values from that given by the expression is a matter of some conjecture, but they believe its use is justified for a rough approximation for the larger ions. Using Bridgman's (1) value of the coefficient $\frac{1}{V^0}\left(\frac{\mathrm{d}V}{\mathrm{d}T}\right)$ as 3.2×10^{-4}, the integration of equation 5 becomes

$$\Delta S = -22\,\frac{e}{r}\text{ cal. per degree per mole} \tag{7}$$

where the constant is for the reaction involving no change of entropy with volume, i.e., for 1 mole of ions in 24.4 liters of solution at 25°C. A test of equation 7 with a number of ions is given as table 4.

The agreement is not very good in several of these examples and is still worse for the smaller ions, as might be expected from an assumption regarding the electrical pressure. However, when we recall that the calculation involves only two experimental constants for water and our previously chosen effective radii, it does give considerable justification for our picture of the entropy of hydration as due to the compression of the water about the ions by the electrostatic field. The determination of ionic entropies in other solvents would help to solve many of these problems and would give a much more complete understanding of ionic solvation. However at present the solubilities, activity coefficients, and heats of solution of salts in non-aqueous solvents are too meager to permit the calculation for even a single case.

TABLE 4

A test of equation 7

ION	S_{gas}	$\bar{S}_{1M}$	$\bar{S}_{absolute}$ 1/24.4 molal	EFFECTIVE RADIUS	ΔS	
					Exptl.	Equation 7
Na^+	35.4	10.1	16.5	1.65	18.9	13.3
K^+	37.0	20.0	26.4	2.03	10.6	11.0
Br^-	39.0	24.0	30.4	1.95	8.6	11.3
Cl^-	36.7	18.1	24.5	1.81	12.2	12.1
I^-	40.5	30.3	37.0	2.16	3.8	10.2
Ba^{++}	40.7	−8.4	−2.0	2.05	42.7	43.0

There are still a fairly large number of aqueous ions for which we have not obtained entropy values. Some of these, as for example phosphate and chromic ions, are difficult to determine, because hydrolysis corrections are large and heats of hydrolysis are not accurately known. In other cases, such as the rare earths, heats of solution and activity coefficients must be obtained. The paramagnetic ions are difficult, since it is necessary to to carry the specific heats measurements to much lower temperatures in order to avoid errors which may arise from low temperature transitions and errors in extrapolation. For example, we have a complete specific heat curve for ferrous oxalate from 298° to 14°A., but at the latter temperature the curve is still far from obeying the T^3 law. However we believe that most of these experimental problems will be solved in the next few years, and that many new ions will be added to our table of ionic entropies.

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DISCUSSION

Dr. Onsager suggested that the entropy of an ion could be computed theoretically as the temperature coefficient of the work required for charging.

Dr. Latimer answered that the entropy deficiency expected on this basis would amount to about one-third of the observed effect.

Dr. Onsager emphasized the importance of this disagreement. Any satisfactory theory of ionic entropies must take into account the anomalous dielectric properties of the solvent in the neighborhood of an ion.

METHODS FOR THE THERMODYNAMIC CORRELATION OF HIGH PRESSURE GAS EQUILIBRIA WITH THE PROPERTIES OF PURE GASES[1]

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I. THE GENERAL LIMIT METHOD

The general limit method is an exact thermodynamic method, but requires a knowledge of the properties of gas mixtures, as well as of pure

Ordinary thermodynamics gives us partial differential equations for the variation of thermodynamic functions with pressure or volume at constant temperature and composition. By integration of such equations we can determine the value of any desired function at a finite pressure in terms of an integration constant, which represents its value when the system is in the initial state. If we take this initial state at infinite volume and assume that the system at infinite volume has the properties of ideal gases, we can eliminate the constant of integration, thus arriving at a formal solution of the problem.

For an understanding of this method it is necessary to know that when we calculate the relative value of a thermodynamic function by means of integration with respect to several variables the order of the integrations makes no difference in the final result, and we can choose the most convenient order. This is to make the pressure or volume integration at constant temperature and composition, and to make it last in the sequence.

We know that a system of real gases at infinite volume does not in all respects resemble a system of ideal gases. For instance, the volume change on mixing real gases at constant temperature and pressure does not in general approach the ideal gas value—zero—at zero pressure, but a finite value. Since the entropy and the two free energies become infinite like the volume, a similar finite difference between the ideal gas and the infinitely expanded real gas might reasonably be feared in these cases also. In any event, the limit method sketched above leads immediately to "infinite" integrals[2] which must be eliminated before any actual calculation can be made.

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[1] Contribution No. 357 from the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Van der Waals (45) used the limit method to calculate the Helmholtz free energy of a mixture of van der Waals gases. Van Laar in 1901 (29) stated what changes are necessary in the expression for the entropy of a mixture of ideal gases, in order to obtain an equation for substances in any state of aggregation, and proceeded to deduce a general mass-action law. It is obvious now that his formal expression could have been justified by the use of the limit method, leaving only the infinite entropies and integrals to be discussed. In his paper with Lorenz in 1925 (31), however, he applied the limit method only to the energy, and obtained the entropy expression by correcting the ideal gas expression for the "free volume" of the gas mixture, stating that a rigorous derivation of the entropy expression would be published in full elsewhere.

So far as the writer can discover, none of the immediate successors of van der Waals has brought the general limit method into a form suitable for actual calculation, nor has removed the difficulty of the infinite entropy or eliminated the infinite integrals and their partial derivatives.

This seems to have been done first by the writer in 1925 (19), by means of the assumption that the equilibrium pressure, p_1, of a gas in a mixture[3] becomes equal to the product of the total pressure, p, by the mole fraction, x_1, of the gas, as the pressures are indefinitely reduced at any temperature. This must of course be understood to mean that the ratio p_1/px_1 approaches unity at zero pressure. Indeed, according to the very logical development of J. A. Beattie (8), this ratio should be expressible as unity plus a power series in p beginning with the first power of p and having bounded coefficients, i.e., not infinite. With the aid of this assumption the following general equation was deduced for the fugacity, f_e, of a gas in a mixture

$$RT \ln f_e = \int_0^p (\bar{v}_1 - v_1)\, dp + RT \ln f_p + RT \ln x_1 \qquad (1)^4$$

where $\bar{v}_1$ is the partial molal volume of gas 1 in the mixture at the variable pressure p, v_1 its molal volume at p, and f_p is the fugacity of gas 1 at the upper limit,—the pressure of the mixture for which f_e is calculated. This isothermal relationship, taken together with the treatment of fugacity by Lewis and Randall, solves in principle mass-action problems at constant temperature. With the aid of certain thermal data, problems involving change of temperature may also be solved.

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[2] Whose integrand, or one of whose limits becomes infinite.

[3] The pressure of the pure gas when in equilibrium with the mixture through a semipermeable membrane.

[4] In accordance with a statement in the paper (19), zero has been placed in the lower limit instead of the p^* originally printed.

Starting with the above assumption and the second assumption that the *energy* of a pure gas is expressible at any temperature as a similar power series in the pressure—both are isothermal assumptions—Beattie (8) has given a very complete and logical treatment of the thermodynamics of gases and gas mixtures along classical lines, which includes a theoretical basis for the determination of thermodynamic temperature by gas thermometry.

It is known that the integral of equation 1 is not infinite or zero (22). With regard to the possible finite difference between the infinite entropy of mixtures of real gases and of ideal gases at infinite volume, it can be proved (23) from equation 1 that the entropy and also the free energy changes on mixing real gases at constant temperature and pressure are the same in the limit at zero pressure as for ideal gases (8). Equation 1 can be applied without further hypothesis in case there are enough data relating to the volumes of gaseous mixtures.

The thermodynamically equivalent relation (2)

$$RT \ln f_e = \int_0^p (\bar{v}_1 - RT/p)\, \mathrm{d}p + RT \ln p x_1 \qquad (2)$$

was later derived by the writer (21), by Gibson and Sosnick (18), and also by van Lerberghe (35) (except that the infinite integral was not yet removed), and was applied empirically by Gibson and Sosnick to the extensive data of Masson and Dolley (38) on the volumes of mixtures of ethylene and argon. Similarly Merz and Whitaker (39) applied equation 2 to the data of Bartlett (1).

These calculations were not really wholly empirical, as in the absence of complete data these authors assumed that the integrand was not only finite but also zero at zero pressure, which is not the case for the given mixtures, according to the writer (22). As there was no immediate chemical application for the fugacities thus calculated, the calculations represent in a sense one-half a typical thermodynamic correlation.

The methods now to be discussed are special methods, which, containing hypotheses about gaseous mixtures, do not require for their application any gas-mixture data, and are the methods promised in the title.

II. THE METHOD OF GIBBS

Gibbs showed (17) that the law of Dalton in the comprehensive form given by Gibbs and its thermodynamic consequences are consistent and possible for a mixture of gases which are not ideal gases and indeed without any limitation in regard to their individual thermodynamic properties.

His proposition—that the chemical potential of a gas in a mixture will be equal to the potential of the same gas when pure and at the temperature and concentration which it has in the mixture—gives a solution of the problem. This solution is very convenient in certain cases, but implies that the Gibbs-Dalton law holds throughout the pressure range. Using the general limit method, and assuming that this law holds at infinite volume, the author (24) showed that it will apply at all pressures if the pressures are additive at constant volume.

This method of Gibbs has been applied only in a few examples of what we may call the vapor pressure problem: by Lurie and Gillespie (37) to their data on mixtures of nitrogen and ammonia in equilibrium with barium chloride ammine, and essentially by Cupples (11), who developed independently by means of interesting physical reasoning a method of calculation—which is the same as the Gibbs method—and applied it to the data of Larson and Black (33) on mixtures of ammonia, hydrogen, and nitrogen in equilibrium with liquid ammonia. The writer (24) compared the calculated with the measured values of the mole fraction of ammonia in the equilibrium gas mixtures, for both sets of experiments, and stated that the deviations of the Gibbs-Dalton law are in all cases smaller than those of the ideal gas form, but the improvement is not in most cases impressive.

Gerry and Gillespie (15) found in the calculation of the normal vapor pressure of iodine from the data of the gas-stream method that the errors of the Gibbs method are of the same order of magnitude and in general slightly greater than for the common assumption that the vapor pressure, corrected for the effect of total pressure, equals px_1 at the experimental pressures.

In terms of fugacities, the Gibbs-Dalton law states that the fugacity, f_e, of a gas in a mixture equals the fugacity of the pure gas at the temperature and concentration of the gas in the mixture. This is evident because the chemical potentials are then equal. The limit method gives the general equation

$$RT \ln f_e = \int_{\infty}^{V} (\mathrm{d}p_1/\mathrm{d}n_1 - \mathrm{d}p/\mathrm{d}n_1)\,\mathrm{d}V + RT \ln f_{1c} \qquad (3)$$

where the first derivative is for the pure gas at the molal volume V/x_1 and the second is for the mixture at the average molal volume V; the upper limit is the average molal volume of the mixture at the pressure and temperature for which f_e is calculated. The derivatives are partial, being taken at constant volume and temperature, and without variation of any mole numbers except for gas 1.

Putting the integrand of equation 3 equal to zero can be shown equivalent to announcing additivity of pressures. This equation is given only to show an analogy with the Lewis and Randall fugacity rule; other analogies have been given elsewhere (24).

In applying the method, the pressure of a pure gas must be determined for the same concentration as it has in the mixture. Since this concentration, in the case of the vapor pressure problem, often exceeds the concentration at the normal vapor pressure, a certain degree of extrapolation into a metastable region is required. This is however much less than for the next method.

III. THE METHOD OF LEWIS AND RANDALL

This is based on a suggested rule (36) that the fugacity of a gas in a mixture equals its fugacity when pure, and at the temperature and total pressure of the mixture, multiplied by its mole fraction in the mixture. They stated that the rule implies the additivity of volumes at constant pressure and the additivity of heat content. Using the general limit method, and assuming that this rule holds at infinite volume, the author (19) showed that it will hold at all pressures if the volumes are additive. A little consideration of equation 1 supplies the proof.

The method is particularly convenient in studying the variation of the equilibrium constant with pressure. The first real test of the rule by chemical data was by the author (21), in which the Haber equilibrium data of Larson and Dodge (34) were correlated with the pressure data for the pure gases with the aid of the Keyes equation of state. It was concluded that the Lewis and Randall rule is verified excellently to 50 atmospheres and well at 100. Available constants in the Keyes equation of state were sufficient to determine the last two coefficients in the very simple equation

$$\log K_p = A/T - B - Cp/T + Dp/T^2 \qquad (4)$$

The first two coefficients reproduce the absolute value of log K_p at zero pressure over the temperature range, and had been determined empirically by the author (20).

The results of this simplified equation were substantially identical with the results obtained by exact integrations with the aid of the complete Keyes equation of state. Furthermore, different values for the equation of state constants as obtained by different authors led to equally satisfactory agreement with the experimental data. It is evident that "the danger of the use of an equation of state of imperfect accuracy for calculations of such functions as γ"—the ratio of the fugacity to the pressure—as feared by Newton (40) can easily be overestimated.

Newton and Dodge (41) have recently applied the Lewis and Randall rule again to the Haber equilibrium data, using for the pure gases the fugacity graphs of Newton (40) with good results.[5]

The practical significance of the success of the Lewis and Randall rule is twofold. First, the enormously important effect of pressure upon the yield of a chemical reaction can be calculated reasonably accurately at pressures not too high. Second, as pointed out already (21), such success means that the equilibrium constant will not vary greatly with composition at constant temperature and pressure, and hence not much improvement of yield can be expected in the use of unstoichiometrical ratios of reactants.

On the other hand, success in the calculation of the equilibrium constant does not prove the accuracy of the separate fugacities found for the several gases involved in the reaction, since compensation of errors can and does occur in this calculation, and the writer (19) therefore proposed to study simpler systems in which no compensation is possible, such as barium chloride ammine in equilibrium with ammonia admixed with an inert gas.

In the application of the method to the vapor pressure problem the integral of $(v - RT/p)dp$ has to be determined from zero to the total pressure of the mixture. If the phase emitting the vapor is a compound the method can be applied without extrapolation, until the total pressure reaches the normal vapor pressure. As thus applied by Lurie and Gillespie (37) to their data it gave good results. On the other hand, if the phase emitting the vapor is a practically pure liquid or solid, vaporizing without decomposition, a serious degree of extrapolation will be required. Gerry (14) found the results of the method "extremely bad for cases of condensible substances at small mol fractions," as illustrated by the case of iodine vapor mixed at 1 atmosphere with air, hydrogen, or carbon dioxide. The errors here were from 3 to 8.7 per cent, much worse than the ordinary ideal gas treatment—whose errors were from -0.7 to $+2.4$ per cent—as judged by the equation of state method.

IV. EQUATIONS OF STATE FOR GASEOUS SOLUTIONS

The contributions of van der Waals to our problem included not only a suggestion of the general limit method and his equation of state for pure gases, but also an important attempt toward an equation of state for gaseous solutions.

He concluded that the equation of state of a mixture of van der Waals gases is itself a van der Waals equation whose constants or parameters can be calculated by relations such as the following for a binary mixture:

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[5] No stress should be laid on the fact that their results at 300 atmospheres are better than those of the writer, as the contrary is the case at 100 atmospheres, and their deviations are changing sign between 100 and 600 atmospheres.

$$\begin{aligned} b &= b_1x_1^2 + 2b_{12}x_1x_2 + b_2x_2^2 \\ A &= A_1x_1^2 + 2A_{12}x_1x_2 + A_2x_2^2 \end{aligned} \tag{5}$$

in which the interaction constants b_{12} and A_{12} are not predicted by theory and may have to be determined from data as adjustable constants. Various authors have used simplifying assumptions such as the relations 6 and 7:

$$b = b_1x_1 + b_2x_2 + b_3x_3 + \ldots\ldots \tag{6}$$

$$A^{1/2} = A_1^{1/2}x_1 + A_2^{1/2}x_2 + A_3^{1/2}x_3 + \ldots\ldots \tag{7}$$

which enable the calculation of the constants or parameters of the mixture equation, for any number of components, from the equations of the pure gases, without the introduction of arbitrary constants.[6]

For an account of the early work on these suggestions reference is made to the paper of Beattie and Ikehara (9). They state "because of the failure of van der Waals' equation to give even an approximate representation of the compressibility of pure gases over a wide range of temperature and density, it has never been applied to compressibility data on gas mixtures except[7] at relatively low pressures."

It has already been emphasized (19) that a determination of the mixture equation, taken together with the general limit method, will bring with it a complete solution of the mass-action law for compressed gases.

For convenience, the relations 6 and 7 will be designated hereafter as linear combination of parameters, in spite of the fact that the combination rules are theoretically derived from the quadratic relations 5.

F. G. Keyes suggested (see Gillespie (19)) that the equation of state of a mixture of Keyes gases is of the Keyes form, and that the constants for the mixture can be determined by applying equation 7 to the A constant and equation 6 to the remaining constants.

As will be mentioned later, Lurie and Gillespie (37) applied this suggestion in connection with the general limit method to their equilibrium data on mixtures of ammonia and nitrogen with very good results and also to the previous equilibrium data of Pollitzer and Strebel (42) on mixtures of nitrogen and carbon dioxide with very good results to 80 atmospheres at 0°C. and to 50 atmospheres at −51.6°C. More recent tests by means of equilibrium data will be discussed later.

Keyes and Burks (28) measured the compressibility of mixtures of nitrogen and methane to about 300 atmospheres and from 0° to 200°C. and found that the constants in the Keyes equation for the mixtures could be satisfactorily calculated by means of this combination of parameters.

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[6] Relations 6 and 7 imply that b_{12} is the arithmetic mean of b_1 and b_2 and that A_{12} is the geometric mean of A_1 and A_2.

[7] See, for instance, Trautz and Emert (43), Trautz and Narath (44), and Eucken and Bresler (13).

Beattie (5) found that the pressures of the nitrogen–methane mixtures of Keyes and Burks are well represented by the Beattie–Bridgeman equation of state when the A constant is calculated by equation 7 and the others by equation 6.

For other methods of attack on the problem of equations of state for gas mixtures, which have not yet been applied extensively to chemical data, reference will be made only to the paper of Beattie and Ikehara (9).

V. THE CALCULATION OF VAN LAAR

In discussing the experimental work of Bartlett (1), who found very much more water vapor in a mixture of nitrogen and water vapor in equilibrium at high pressures with liquid water than can be explained by the long-known effect of pressure on vapor pressure as given by the Poynting relation, van Laar (30) states in 1929 "we have repeatedly given the exact solution of this problem, the last time in 1928 in this journal."[8]

He assumes as in 1901 that the constant-volume heat capacity of the gas is constant at infinite constant volume. For thermodynamic correlations over an extended temperature range this should undoubtedly be replaced with a series expansion in the temperature, and there is no objection to this on the basis of the general limit method. The thermodynamic derivations of van Laar are based on the van der Waals equation with constant A and b, but in the application of the resulting equations the A constant, which alone enters the final result, is recognized as variable with temperature and pressure, and a value is used for the experimental temperature and pressure.[9] These distinguishing features of the calculation are retained in other papers by van Laar and appear characteristic of his method of attack.

He computes the A constant for water from the heat of vaporization, corrects the A value of nitrogen given by van der Waals for the difference of temperature and pressure, and combines these A parameters according to equation 7. He is able to calculate essentially the mole fraction of water in the gas mixture in equilibrium with the liquid within about 2 per cent of the observed value at the one point studied,—50°C. and 1000 atm.

In conclusion, he states "And herewith we have indeed said everything which is to be said theoretically about this interesting problem." This need not be taken to indicate any estimate of the previous American work, particularly the calculations of Lurie and Gillespie on the data of Pollitzer and Strebel, as none of this work is mentioned by him. It refers probably to certain experimenters who did not realize that the px_1 product for a gas mixture in equilibrium with a condensed phase emitting the gas 1 need not theoretically be equal to the vapor pressure after this is corrected for the total pressure by the Poynting relation.

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[8] Z. physik. Chem. **137A**, 421 (1928); see also Z. anorg. allgem. Chem. **171**, 42 (1928).

[9] Instead of for some average value of the pressure. Really there would be an integration from zero to the final pressure, were the variation in A introduced in the beginning.

This theoretical lack of equality is shown by the calculations of van Laar. It had been shown in a general manner by Lurie and Gillespie that the lack of equality is a necessary consequence of the fact that the laws of Boyle and Avogadro fail at the experimental pressures. This follows from their proof[10] that these laws must hold if such equality holds for various values of p and x_1 at any given constant temperature.

VI. THE EQUATION OF STATE METHOD AND ITS APPLICATIONS

We have seen that the general limit method furnishes equations which need integration. An equation of state for mixtures, obtained by combination of parameters, permits the integration, either graphically—as in the case of the Keyes equation—or explicitly in terms of simple functions—as in the case of the Beattie–Bridgeman equation. Such integration of the equations of the limit method gives us what we may call the equation of state method. It is special, like those of Gibbs and of Lewis and Randall. The method of Gibbs involves addivity of pressures; that of Lewis and Randall, the additivity of volumes; and the equation of state method involves a kind of additivity of equation of state constants. It is of course true that additivity of pressures or of volumes furnishes at once the equation of state of mixtures in terms of the equations for the pure gases, but this circumstance need not be the occasion of any confusion in our use of the term "equation of state method," especially since it is only for this method that equations of state are indispensable.

The equation of state method furnishes useful if not indispensable aid in the empirical application of the general limit method. As a matter of fact, neither this latter method, nor the method of Lewis and Randall, can be applied purely empirically. There are integrals to be found—under curves that must be extrapolated from the experimental region to the axis of zero pressure—and for this extrapolation some hypothesis must be used, such as (1) that the limit intercept is zero, or (2) that the experimental curves should be continued to the axis without introduction of new curvature, or (3) that the limit intercept and its slope at the axis can be found for the general limit method by combination of parameters and for the Lewis and Randall method by the use of the individual equations of state. The first assumption was tacitly made by several authors, as mentioned above, but the writer showed (22) that in application this violated both the second and the third, which were together in agreement. A judicious use of equations of state is therefore recommended even to those aiming at pure empiricism in the treatment of data, whether for mixtures of gases or for pure gases.

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[10] Later repeated more fully by the writer (24).

As mentioned above, the equation of state method was applied by Lurie and Gillespie to their data on mixtures of ammonia and nitrogen in equilibrium with barium chloride–barium chloride octammine. They found a good agreement of computed to experimental values, possibly within the uncertainty of the latter. They applied the method also to the previous data of Pollitzer and Strebel on the compositions and pressures of nitrogen and carbon dioxide in equilibrium with liquid carbon dioxide, with very good agreement at 0°C. to 80 atmospheres and at −51.6°C. to about 50 atmospheres. For these calculations they used the Keyes equation of state. Later calculations of Dr. Eli Lurie (unpublished) showed that when the Beattie–Bridgeman equation is used for mixtures linear combination must not be applied to the first power of the *c* constant—because of its large value for ammonia—but may be applied to its square root.

Keyes (27) developed equations for chemical equilibria in non-ideal gases whose isometrics are linear, starting with an entropy expression derived from a consideration of the modifications of the ideal gas result necessary in such a case. As the entropy expression is consistent with that derived from the limit method the results are treated in this group. Comparison of the results with the experimental data of Larson and Dodge (34) and of Larson (32) showed tolerable agreement to 600 atmospheres, and agreement as to order of magnitude throughout.

Gillespie and Beattie (25) undertook to correlate all the Haber equilibrium data with respect to both temperature and pressure. Empirical equations for the heat capacities of the pure gases as functions of the temperature at infinitely low pressures were deduced from 1 atmosphere values by means of a relation given by Beattie (6), and the general limit-method was applied with the use of the Beattie–Bridgeman equation of state of mixtures. Instead of using the empirical two-constant equation of Gillespie (20) for K_p at infinitely low pressure, a new equation was derived containing terms from the known heat capacities and two adjustable constants, determined from the whole body of data. They compared the experimental with the calculated percentages of ammonia in the equilibrium mixtures and found an agreement within the experimental error over the whole field of temperature and pressure. The deviations are small, and the deviation plot shows no significant trends in the deviations.

Newton and Dodge (41) have recently stated: "however, they do not strictly calculate the high pressure equilibrium constants from the low pressure ones, but rather leave two adjustable constants in their final equation and select their values to fit the data best." Without explanation, this statement may prove very misleading. It ought therefore be emphasized, that the two adjustable constants were used substantially in the same way as the two used by Newton and Dodge, not being used at all in the calculation of the pressure effects. Furthermore, a recent examination of the published papers shows that Gillespie and Beattie would not have found a less satisfactory agreement with the limited field of data considered by Newton and Dodge if they had in fact used the same empirical equation and constants as were used by the latter authors, but on the contrary a slight over-all improvement, which would have been gained at the expense of the agreement with the high temperature data of Haber.

The pressure effects were in fact calculated from existing equation of state constants without any use or benefit of arbitrary constants, and if, for example, the equilibrium constant is known at one temperature and pressure and the heat effect of the reaction similarly known at one point, then calculations similar to those of Gillespie and Beattie will reproduce the whole body of equilibrium data, which extend at 30 atmospheres from 325° to 952°C. and at some temperatures from 10 to 1000 atmospheres. The superior results given by their method over those given by the Lewis and Randall rule is not due to a better management of the two necessary adjustable constants, but to the known superiority of combination of parameters over the rule of additive volumes. Likewise, these results serve to verify the precision of the equilibrium data[11] and thus to show that the discrepancies introduced by this rule of additive volumes are real and of chemical significance.

Gillespie and Beattie further calculated the entropy constants of ammonia, nitrogen, and hydrogen, and the heat effect ($-\Delta H$) of the Haber reaction as a function of pressure and temperature. With the aid of the papers of Beattie (4, 7, 8) all numerical values for any desired thermodynamic function can be calculated for these gases, severally or in mixtures.

Again, they calculated (26) the optimum hydrogen:nitrogen ratio for ammonia formation in the Haber equilibrium. At, for example, 500°C. and 1000 atmospheres the best ratio, when argon is absent, is not 3, as would be the case according to the ordinary mass-action law and according to the Lewis and Randall rule, but 2.91 in the initial reactant mixture and 2.68 in the final equilibrium mixture. When argon is introduced with the nitrogen in the usual amount, the ratio of hydrogen to (pure) nitrogen is not 3.036, as would be the case according to the ordinary mass-action law, but 2.92 in the initial and 2.72 in the final mixture. The corresponding improvement in yield that could be realized by the use of optimum rather than stoichiometrical ratios turns out however to be insignificant—only about 0.03 to 0.04 per cent ammonia, when the final mixture contains about 58 per cent ammonia. On the other hand, if the yield at a ratio of say 3 were to be calculated from the actual yield at a quite different ratio, the error of the ordinary mass-action law, even at constant temperature and pressure, might easily be important.

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[11] Actually, their calculated percentages of ammonia agree better with the measured values than will percentages calculated from the K_p values given by the experimenters, since these used an approximate relation for finding K_p which has less precision than the data warrant.

In all these calculations the first power of the c constant was combined linearly, instead of the square root, as is now believed better. (When the constants are small, or the temperature high, the difference is slight.) Professor Beattie has studied the differences made in the former calculations of the equilibrium constant when the root of c is combined, and finds that they are small,—the recalculated values fit the data as well as the previous values, the deviations being simply distributed differently among the points.

In the determination of normal vapor pressures from the data of the gas-stream method it becomes necessary to make a correction for the failure of the ideal gas laws. When equation of state constants are available for all the substances concerned, the problem is like the vapor pressure problem previously discussed. In the case of iodine, there are no pressure–volume–temperature data from which such constants can be deduced. Braune and Strassman (10) obtained gas-stream data for iodine, using two different inert gases, hydrogen and carbon dioxide, and worked over a field of temperature and pressure. Gerry and Gillespie (15) showed that these data could be used to determine the constants A_0, B_0, and c in the Beattie–Bridgeman equation of state, as simplified for low pressures, and the results in turn used to calculate the normal vapor pressure of iodine from the very accurate measurements of Baxter and his coworkers (2, 3). The effect of the correction for the failure of the ideal gas laws as applied at 1 atmosphere was found decidedly important, compared with the precision obtainable in the best measurements. A simple equation for the vapor pressure of iodine as a function of the temperature was given. This utilizes their pressure corrections and the temperature smoothing by Giauque (16) of the Baxter data by means of spectroscopic and specific heat data.

In most previous cases of a solid or liquid evaporating into a gas mixture, the experimenters have found more evaporated substance at equilibrium than they expected from the ordinary assumption that the vapor pressure (corrected for total pressure) is equal to the px_1 product, and they have therefore spoken of a solvent effect. In the case of iodine, the results for air and for carbon dioxide at the experimental temperatures were in this same sense, but the results for hydrogen were opposite.

VII. CONCLUSION

Corresponding to a greater activity of experimenters in the study of chemical and physical equilibria involving gas mixtures at high pressures, and to renewed attacks on the equation of state problem, there has been in the last few years considerable progress in the thermodynamic correlation of the results of equilibrium studies with equations of state and thermal data. Much of this has been with the aid of equations of state for mixtures, deduced from equations for the pure gases by means of a rule for combination of parameters.

Although an exact solution of any of the problems is complicated, in many cases solutions are possible by means of simple equations, obtained by omission of terms of the higher orders.

The only very polar gas involved in a complete correlation is ammonia. Extension to the cases of other polar gases may introduce difficulties, especially at low temperatures. These difficulties appear already in the development of an equation of state for the pure gas. At present the limiting factor in future progress appears to be, not the linear combination of parameters, but the experimental inaccuracy of the equilibrium data and, in some cases, lack of suitable equations of state for the pure gases.

Newton (40) has recently presented fugacity values for a great variety of gases, obtained without equations of state, and some of these were used by Newton and Dodge (41) in connection with the Lewis and Randall rule, as mentioned above. In order to use them in connection with the Gibbs method it would be necessary to know the molal volumes of the pure gas at certain important pressures. In order to use such fugacity values in connection with corrections of the Lewis and Randall rule, found from linear combination of parameters, it would of course be necessary to have equation of state constants for the various pure gases. But it would not be necessary to have these with the same accuracy as would be necessary for calculation of the fugacity values themselves; and it may be that some approximate calculation of the constants—for instance, by van der Waals theory from critical data—will in some cases be good enough for the purpose of calculating the correction terms.

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ULTRAFILTER MEMBRANES AND ULTRAFILTRATION

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I. INTRODUCTION

A. TERMINOLOGY

An *ultrafilter* is defined as a filter whose pores or interstices are of colloidal or molecular dimensions; filtration through it, ordinarily with the purpose of complete or partial retention of the colloidal or molecular species present in the disperse system filtered, is termed *ultrafiltration.*[2]

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1. *Diffusion, dialysis, osmosis, and ultrafiltration*

The distinction between ultrafiltration and other closely related phenomena is illustrated by the following familiar model. A vessel is divided by a membrane into two compartments, of which one is occupied by an aqueous solution, molecular or colloidal, and the other by pure water. Owing to the concentration gradient across the membrane, the water will tend to diffuse into the solution, and the solutes into the water compartment. If the membrane pores are large compared with the diameters of all solute particles present, so that no specific steric hindrance is offered to the latter, both processes take place at relative rates the same as in *free diffusion.* The only effect of the presence of the membrane (apart from electrokinetic influences) is a reduction of the area through which diffusion can occur, and, in case the pores do not run perpendicular to the membrane surface, a prolongation of the path traversed by the diffusing molecules. If, however, the pore sizes are of the same order of magnitude as the solute particle sizes, the solute encounters a preferential resistance; this may include a simple viscous drag as represented by the Ladenburg correction to Stokes' law (175a), specific molecular interaction, or electroviscous effects. Such diffusion may be termed impeded. *Dialysis* is a differential diffusion, employing a membrane impermeable to the colloidal solutes but permeable to the crystalloidal. The latter diffuse into the water, while the water diffuses into the solution. In dialysis under pressure, the solution is under sufficient pressure so that the hydrodynamical flow of water out of the solution balances the molecular diffusion into it, and the concentration of the colloidal solutes remains unchanged while the diffusible solutes escape. If the membrane is impermeable to all solutes, so that the only diffusion occurring is that of water into the solution, the process is ordinary *osmosis.*[3] At osmotic equilibrium, the solution is under a hydrostatic pressure (the osmotic pressure) which causes sufficient flow out of the solution to balance the molecular diffusion of water into it.[4] Now, if the hydrostatic pressure is increased beyond the osmotic pressure, there is a net flow of water out of the solution compartment, with a concentrating of the solute, and we have *ultrafiltration.* Similarly, in dialysis under pressure, if the pressure is increased so that both water and diffusible solutes flow out of the solution, the experiment becomes one of ultrafiltration.

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[2] For brevity, the prefix *ultra* is frequently omitted in this paper.

[3] Dialysis may also be considered as osmosis in the presence of diffusible constituents. This complex process has been discussed by Schreinemakers (252, 253).

[4] Osmotic equilibrium in the presence of diffusible constituents may involve a Donnan membrane equilibrium (50).

Under actual conditions of ultrafiltration, the hydrodynamical flow through the membrane due to the applied pressure is usually so much greater than any diffusion effects that the latter may be considered negligible.

2. Porosity and permeability

The term "permeability" has been frequently used to characterize ultrafilters, as a measure of the size of the pores or interstices in the filter structure. The terminology adopted in this paper, and suggested for general use, designates *porosity* to describe the filter structure, and *permeability* for reference to its behavior in diffusion or filtration of a disperse system. For example, a membrane of given porosity will show varying degrees of permeability to a certain protein depending on whether the experiment is one of diffusion or ultrafiltration, and, in the latter case, on a host of physical factors including the pH, the rate of filtration, and the concentration of the solution.

B. HISTORICAL SURVEY

The study of ultrafiltration has always been closely associated with that of dialysis, and, to a lesser extent, osmosis and the problem of the semipermeable membrane.

Dialysis experiments through artificial membranes of collodion were recorded by Fick (120) in 1855. The first mention of the process now known as ultrafiltration appears to have been by Schmidt (248) in 1856, who found that, when a solution of protein or gum arabic was filtered through an animal membrane, the filtrate was less concentrated than the original solution. Similar observations were made by Hoppe-Seyler (157). Schumacher (254), in 1860, described the collodion sac for dialysis, and Sanarelli (246) introduced it in 1891 for bacteriological work, including ultrafiltration of blood plasma *in vivo*. In 1896, Martin (211, 211a) used a bacteriological candle impregnated with gelatin or silicic acid as an ultrafilter to separate colloids from crystalloids. Borrel and Manea (51) and Malfitano (199) used collodion sacs for ultrafiltration in 1904, and Levy (177), in 1905, ultrafiltered enzymes and showed that dialysis and ultrafiltration did not arrive at the same result.

The classic papers of Bechhold (16, 17, 18), who coined the term "ultrafiltration" in 1906, represented the first systematic study of this subject. By impregnating filter paper with acetic acid collodion, Bechhold prepared the first series of membranes of graded porosities; he was the first to estimate critically the pore sizes in his filters, and first pointed out the rôle of adsorption and other physical factors in the filtration process. In the next twenty years, numerous workers experimented in ultrafiltration and introduced various types of ultrafilters and various methods for grading the porosity (see part II). Among these may be mentioned Bigelow and Gemberling (45b), who, in 1907, prepared flat collodion membranes from ether–alcohol solution, and Zsigmondy and Bachmann (294), who patented in 1918 a graded series of membranes to be manufactured by a similar process. Meanwhile, ultrafiltration technique had been adopted by bacteriologists and physiologists, who employed it in attempts to estimate the particle size of enzymes, toxins, and viruses, and to construct models of vital processes involving membranes.

Ultrafilters, and semipermeable membranes generally, were regarded by some early authors as mechanical sieves, so that permeability was a matter solely of particle dimensions and pore dimensions. The opposite extreme in explaining semipermeability was reached by the capillary attraction theory (45a, 272, 284), which represents the solvent as strongly adsorbed in the pore and transmitted by surface mobility of the adsorbed molecules; and by the theory of partial solubility (179a), which represents the solvent as dissolving into the membrane on one side and out on the other. These theories would, however, predict specific effects dependent on the nature of solute and solvent, whereas the experiments of Duclaux and Errera in 1924 (82, 83) demonstrated the sieve-like behavior of membranes in the flow of various liquids through them, and the work of Collander in 1926 (75) showed that the rate of impeded diffusion of crystalloidal molecules through membranes depended principally on the molecular volume and not on the nature of the diffusing solute. On the whole, there is adequate support for the viewpoint that the fundamental mechanism in ultrafiltration is sieving, modified by adsorption, blocking, and other effects arising from the very large ratio of pore length to pore width and of pore surface to cross-section area in all ultrafilters.

The most significant recent developments in ultrafiltration have been the extensive study by Manegold and collaborators of the structure of collodion membranes, and the introduction by Elford (93) in 1930 of the most satisfactory graded series of collodion membranes yet developed. These filters have been successfully employed by Elford and collaborators to estimate the sizes of particles in a number of biological systems.

C. PRESENT PROBLEMS OF ULTRAFILTRATION

The applications of ultrafiltration to chemical, as well as to biological, problems are twofold: fractionation and study of the composition of disperse systems, and estimation of the particle sizes in disperse systems.

The simplest example of the first type of problem is the preparation of a colloid-free ultrafiltrate from a sol. This is of value in the study of lyophobic colloids (195) and lyophilic colloids (188) alike, and especially in biological investigations, where much attention, for example, has been given to protein-free ultrafiltrates of blood serum and plasma. Ultrafiltration also permits obtaining the disperse phase in solid form, if desired. An example of the removal of particles of a different order of magnitude is the sterilization of bacteriological systems by ultrafiltration, whose methods are often superior to those involving the use of porcelain candle filters. Water and solutions of inorganic and organic crystalloids may be ultrafiltered to remove stray foreign particles, yielding optically clear filtrates (288a). The applications of ultrafiltration to analytical chemistry, for filtering off colloidal precipitates and the like (as advocated by Zsigmondy and collaborators (296)), have been treated in a monograph by Jander and Zakowski (160). A less simple example of fractionation is the separation of colloidal particles of different sizes. Thus, in a suspension containing bacteria, bacteriophage, and products of bacteriolysis, including a specific soluble substance identifiable by an immunological reaction, suitable filters have served for quantitative separation of the different constituents (66). It has been possible even to effect a partial fractionation of albumin from globulin in serum by ultrafiltration (108). In the case of a polydisperse colloid, successive filtration through membranes of different porosities may fractionate the large particles from the small (16).

The second type of problem—estimation of particle size—is much more difficult and requires a more critical selection of filters and a system of calibration and standardization. It is discussed in part V.

The present paper (a) reviews methods of preparing ultrafilter membranes, of grading porosities, and of calibrating membranes, (b) discusses theoretical and experimental study of the mechanisms involved in ultrafiltration, and (c) reviews experimental application of ultrafiltration to the two types of problems outlined above.

For further discussions of the historical development of ultrafiltration and its applications, reference is made to several reviews by earlier authors (134, 20, 90, 185, 166, 257, 135, 293a, 240, 8); and, in particular, concerning applications to biology, to a recent review by Grabar (141b).

II. Ultrafilter Membranes

A. PREPARATION OF DIFFERENT TYPES OF FILTERS

In any application of ultrafiltration, certain specifications must be set for the filter employed. In the first place, the phenomena which cause the behavior of an ultrafilter to differ from that of an ideal mechanical sieve arise from the high ratio of pore length to pore diameter; and, while it is seldom possible to reduce this ratio below a thousand, it should be limited by choosing the filter as thin as possible. On the other hand, the filter must be mechanically strong enough to withstand the pressure applied in filtration without distortion or rupture. It must be reasonably isoporous, and free from occasional pores which are much larger than the average. It must not, of course, react with or dissolve in any component of the system which is filtered through it. For a fractionation experiment, rigorous control of filter porosity is unnecessary, so long as the pores are large enough to pass the components desired in the filtrate and small enough to retain those desired in the residue. It is for this reason that so many an early experiment, in which no regulation or calibration of filter porosity was made, succeeded in the desired fractionation. It is desirable, however, to calibrate filters rigorously and to have a wide series of porosities available, in order to attain best efficiency by selecting for a given experiment the most highly porous filter which will yet perform the required separation. And, for estimation of particle sizes, a series of carefully calibrated filters covering a wide range of porosities is an essential requirement. For comparative experiments, groups of filters of exactly comparable porosities must be available.

Most ultrafilter membranes are gelatinous, and in the great majority of cases the gel consists of collodion, i.e., nitrocellulose containing about 11 per cent of nitrogen. This gel is produced from a solution of collodion either in glacial acetic acid (acetic collodion) or in a mixture of volatile solvents including principally ether and ethyl alcohol (ether–alcohol collodion). Preparation of artificial gel membranes of reproducible characteristics requires strict adherence to empirical rules in the minor details of technique; this is particularly true of ether–alcohol collodion membranes, but the latter are the most satisfactory if prepared with the required care.

In the following discussion, gelatinous membranes are classified according to whether the gel is impregnated in a supporting structure, or forms its own support. Mention is also made of non-gelatinous membranes. Particular attention is devoted to the types of filters most frequently mentioned in the literature,—those of Bechhold, Bechhold–König, Zsigmondy–Bachmann, and Elford.

1. *Gel membranes impregnated in a support*

a. Support of filter paper or cloth. Collodion membranes impregnated in filter paper were introduced by Bechhold (16), and his simple technique still represents the easiest method of preparing a graded series of ultrafilters. A piece of hardened filter paper is soaked in a solution of nitrocellulose in glacial acetic acid. The excess solution is drained from the paper, and the membrane is gelled by immersion in water. The acetic acid is removed by prolonged washing, leaving a film of nitrocellulose (with perhaps some cellulose acetate) imbedded in the filter paper. The higher the concentration of nitrocellulose in the original solution, the lower the porosity of the membrane (see section B, below). Retention of air by the paper, which might result in microscopic "pinholes" in the final membrane, is diminished by preliminary soaking in pure acetic acid, and practically eliminated by conducting the collodion impregnation in a vacuum. Draining off the excess solution from the paper may leave a layer of irregular and excessive thickness, especially in the case of the more concentrated and hence more viscous solutions; an improved technique involves drawing the soaked paper between rollers of glass or gold-plated nickel before gelation (90, 91).

The chief advantage of the Bechhold membranes lies in the relative simplicity of preparation and the wide range of porosities obtainable (pore diameter from 1 to 5μ down to less than 10 mμ). However, in a given filter, the pore sizes vary over a considerable range (see section C, below), and the limited reproducibility in average pore diameter from one membrane to the next makes comparative experiments difficult, even with rigorous control of experimental technique. Further, the Bechhold filters are rather thicker than self-supporting collodion membranes, and, in contrast to the latter, their thickness increases with decreasing porosity, thus making the ratio of pore length to diameter doubly excessive for the densest membranes.

It is possible also to impregnate ether–alcohol collodion into filter paper, coagulating with water in the same manner (230), but this type of filter has no particular advantages, since ether–alcohol collodion films can be made self-supporting.

Impregnation of collodion in a cloth support has been patented by Duclaux (81), who has also impregnated cloth with cellulose acetate, forming a gel suitable for filtrations with some organic solvents like benzene (80).

b. Refractory support. In some cases, a more rigid support for the ultrafilter gel is employed, such as porcelain, alundum, or metal. Of this type were the earliest impregnated filters, made by Martin (211) by filling the pores of a Chamberland candle of unglazed porcelain with gelatin or silicic acid. The classical "semipermeable" membranes for osmotic experiments, introduced by Pfeffer (233) and developed by Morse and Frazer (217) and Berkeley and Hartley (42), consist of copper ferrocyanide deposited in unglazed porcelain, and have a very low porosity.

The most popular porcelain impregnated filter is that of Bechhold and König, which is a Bechhold membrane with porcelain substituted for filter paper. Crucibles, evaporating dishes, and other vessels, with unglazed bottoms, are impregnated with acetic collodion in the usual way. After use, the nitrocellulose can be burned off. The porosity is varied, as above, by varying the concentration of collodion in the impregnating solution.

Ultrafilters of the Bechhold–König type have been prepared for filtration of non-aqueous solutions. Bechhold and Szidon (37) studied the gelation of collodion and cellulose acetate in different organic solvents, and found the most satisfactory combination to be impregnation by a solution of collodion in ether, followed by coagulation in toluene.

Alundum thimbles have been employed as support for ether-alcohol collodion (54, 238) in ultrafilters and electro-ultrafilters. Collodion has also been impregnated in wire gauze (127), forming a strong filter for use under pressure.

Ultrafilters impregnated in porcelain and the like have the advantage of mechanical convenience and mechanical strength. They are, however, excessively thick, and can remove large quantities of material from filtrates by adsorption. They should be used only for filtration of large volumes of material, where rigid control of membrane porosity is not required, since accurate calibration is difficult.

c. Support of cellophane or collodion. Cellophane, which in itself acts as a very finely-pored, self-supporting ultrafilter, can be given a still smaller porosity by depositing on it a film of cellulose or collodion (190, 191). By filtering through cellophane a solution of cellulose in Schweitzer's reagent, or of ether-alcohol collodion, membranes are obtained which, in filtration of an aqueous solution of sucrose, retain the sugar in varying degrees, and behave as molecular sieves. Membranes of very low porosity have been prepared also by impregnating copper ferrocyanide in collodion films (60a, 49).

2. Gel membranes with a self-supporting structure

a. Artificial membranes. While acetic collodion membranes must be of the impregnated type, owing to the fragility of the acetic collodion gel, membranes made from ether-alcohol collodion have sufficient strength to be self-supporting. These are made in the form of either sacs or discs.

Collodion sacs were the first artificial membranes to be generally adopted (254, 199, 51), and have been used very extensively, especially in biological research. A test tube is filled with a solution of collodion in ether and alcohol, and is inverted and drained, leaving a film clinging to the interior. After evaporation from this film has proceeded for a given time (sufficient for the collodion to set to a gel), the tube is plunged into water; the sac is loosened, removed, and washed free of the remaining solvents. An alternative is to make the sac on the outside of the test tube, rotating the latter to give an even film. Various authors (255, 214, 279, 133, 127a, 164, 71, 131, 276, 79a) have outlined detailed procedures for preparation of sacs, differing in minor points of technique. In particular, Kallós and Hoffmann (162) coated the glass mold with caramel and formed the collodion film on this; on immersion in water, the caramel dissolved, facilitating removal of the sac. Huzella (158) used caramel for forms of various shapes; it could be drawn out in threads for molding minute cylindrical capillaries of collodion. Giemsa (137) formed the sac on a moist thimble of filter paper. The latter, before being dipped into the collodion, was slipped over a perforated cylinder of glazed porcelain, and this formed the filtering apparatus, negative pressure being applied to the inside of the cylinder.

The porosity of collodion sacs is varied by adjusting the ratio of alcohol to ether in the solvent, and varying the time of draining and the duration of evaporation; also by adding small quantities of other reagents to the solution. These added substances may also affect the mechanical properties of the membrane (see part II, B).

The collodion sac is particularly popular because of ease of preparation and the large area available for filtration, and because it constitutes its own container and, unlike the disc, does not require a mechanical holder with clamp and gaskets. It is, however, quite unsuited for work requiring uniform and reproducible ultrafilters. In the first place, the porosity of a given sac is different at different points, tending to be greater at the closed end than at the open end, and it is very difficult to make successive sacs of similar porosities, on account of the high viscosity of the collodion and the rapidity with which the solvents evaporate.

These difficulties may be overcome in making collodion disc membranes, as introduced by Bigelow and Gemberling (45b) and developed by Zsigmondy and Bachmann (294), Bartell and Carpenter (11), Bjerrum and Manegold (47), Pierce (234), and Elford (93) (see also Folley (124) and Snell (260)). A thin layer of collodion solution is poured on a carefully levelled glass plate, a surface of mercury, or a glass plate floated on mercury. Regulated evaporation proceeds, either by diffusion of the solvent vapors into a fairly large draft-free enclosure, or the slow passage of known quantities of air of regulated humidity past the glass plate. Convection shields prevent irregular air currents. The temperature is carefully controlled and maintained constant. After sufficient of the solvents has evaporated, the collodion sets to a gel. The evaporation is prolonged a specified time, and is then ended by suddenly covering the collodion film with water. The remaining solvents are washed free (a process requiring as long as two weeks in some cases—depending on diffusion out of the membrane pores), and the film is cut by dies into numerous small discs.

This is the procedure of Elford (93), which has been redescribed in detail by Bauer and Hughes (15). When proper attention is given to consistency of all details in technique, it is possible to prepare from the same sheet forty discs, which differ in porosity by less than 2 per cent from one another, while successive sheets poured from the same solution of collodion agree in porosity within 10 per cent. The sizes of pores in a given disc vary within comparatively small limits.

The Zsigmondy–Bachmann filters, also, are presumably prepared by a procedure similar to that outlined above. These filters, manufactured commercially by E. de Haen, G.m.b.H., Hannover, and later by the Membranfilter Gesellschaft, m.b.H., Göttingen, are marketed under the names "Membranfilter" and "Ultrafeinfilter." The second firm also prepares membranes of pure cellulose ("Cellafilter"), as introduced by Zsigmondy and Kratz (293b).

It is customary to keep a preservative, such as toluene, thymol, or trypto-flavine, in the water which covers such membranes during washing and storage, since the collodion is particularly favorable to the growth of a mold which enters the pores and completely alters the porosity. The procedure of Elford (93), however, involves a sterile technique throughout, avoiding the presence of preservatives which might have some effect in subsequent filtrations, especially in biological work.

The porosity of collodion disc membranes is varied by the same general methods employed for sacs; these are discussed in section B. Membranes of a very low porosity are prepared by allowing the solvents to evaporate completely from a film of ether–alcohol collodion. Such "dry collodion" films demonstrate even a differential permeability to ions (226, 216a).

Commercial cellophane is a membrane of pure cellulose, with a trace of glycerol. It was formerly possible to obtain grades of cellophane which, when swelled in water, had a porosity of about 4 mμ, and formed very convenient ultrafilters for many purposes (190, 192, 193). McBain and Kistler (190) showed that the water could be replaced, proceeding by way of mutually miscible liquids, by various organic solvents to yield membranes for filtration of non-aqueous solutions. Cellophane of recent manufacture is less porous, and even partially retains sucrose in ultrafiltration. Its porosity may be increased by swelling with concentrated solutions of sodium hydroxide or zinc chloride, but only with difficulty to an extent sufficient to pass sucrose in undiminished concentration (197, 218).

Ettisch and collaborators (116a, 116b) incorporated glycocoll or powdered egg albumin into collodion solutions in order to prepare membranes of mixed ampholyte and collodion. An intimate mixture of protein and cellulose ester was effected by Loiseleur and Velluz (181, 182, 183); a solution of protein in acetic or formic acid was incorporated with an acetic acid solution of cellulose acetate or nitrocellulose, and the mixture employed for impregnation of Bechhold membranes. The porosity, as measured by the rate of diffusion of potassium chloride through the resulting membranes, increased with the proportion of protein.

b. Natural membranes. Various animal membranes have been employed for purposes of dialysis and ultrafiltration, including goldbeater's skin, Bedicher (a membrane from cow's intestine), pig's bladder, fish bladder, amnion, and chorion (45b, 190, 16). These have the advantage of extreme thinness and a consequent comparatively high rate of filtration, but it is difficult to obtain at will a membrane of any desired porosity.

3. Other types of filters

A few types of ultrafilter membranes whose structure is not gelatinous may be cited. Manning (209) plated nickel on 200-mesh wire gauze of nickel or bronze, and thus decreased the sizes of the interstices to give pore diameters of from 50mμ to 300mμ. Warrick and Mack (282) distilled the zinc out of strips of brass, leaving porous copper membranes which showed differential permeability to gases and could serve as semipermeable membranes in the osmosis of aqueous solutions of sucrose. The porosity was evidently very small. Kultashev and Santalov (172a), using a similar procedure, prepared copper membranes permeable to urea and chloride and sulfate ions but not to glucose, and silver membranes permeable to all these crystalloids. Blanc (47a) obtained a porous structure of silica by leaching leucite with strong acid. Prausnitz (236) described ultrafilters of sintered glass, with a mean pore diameter of 1.5 μ. The use of zeolite crystals as molecular sieves has been suggested by Lamb (176), McBain (186), and Pauling (232).

B. METHODS OF VARYING THE POROSITY

An adequate method for grading the porosities of ultrafilter membranes must be capable of varying the porosity continuously, maintaining satisfactory mechanical properties throughout the range. The porosity may be measured in terms of the average pore diameter, as explained in section C.

1. Grading of acetic collodion membranes

The principal method for grading acetic collodion membranes is that originally used by Bechhold,—variation in the concentration of collodion in the impregnating solution. Bechhold (16) found the membrane porosity to be related antibatically with the concentration of collodion, but results were not reproducible from one solution of collodion to the next. In later work, a certain degree of reproducibility has been achieved. The dependence of porosity on concentration, as found by Elford (91), by Krueger and Ritter (170) and Mendelsohn et al. (213), and by Cox and Hyde (76), is shown in table 1. The average pore diameters are quoted as determined by rate of flow of water (part II, D).

Another method for grading is given by Bechhold and Silbereisen (36). The impregnated paper or porcelain, instead of being gelled in water, is immersed in a weak solution of acetic acid; this results in a membrane of considerably higher porosity. Bechhold and Sierakowski (35) pointed out that solutions of collodion in acetic acid, when stored, undergo an aging effect with a marked decrease in viscosity, and that membranes made from aged solutions are more highly porous than the original. The porosity of a membrane is also increased by heating it to 90–98°C. in a water bath, or by denitration by treatment with ammonium sulfide.

TABLE 1

Grading of acetic collodion membranes

PERCENTAGE OF COLLODION IN IMPREGNATING SOLUTION	AVERAGE PORE DIAMETER IN μ			
	Elford (91)	Mendelsohn et al. (213)	Krueger and Ritter (170)	Cox and Hyde (76)
0.5		0.65	0.94	0.82
1.0	0.51	0.32	0.74	0.64
1.5	0.32		0.52	0.40
2.0	0.25	0.12	0.46	0.34
2.5	0.22		0.38	0.26
3.0	0.18	0.11	0.28	0.24
3.5			0.24	0.18
4.0	0.14	0.10	0.20	0.16
4.5			0.16	
5.0	0.09	0.09	0.16	0.10
5.5			0.14	
6.0	0.07		0.14	0.07

2. Grading of ether–alcohol collodion membranes

In the early experiments on ether–alcohol collodion membranes, where the porosity was graded by varying the evaporation times, no quantitative data on porosity were quoted (45, 45b, 279). The more recent work of Bjerrum and Manegold (47) shows, however, that this method is incapable of producing porosities of greater than about 60 mμ. The shorter the evaporation time, the more highly porous the membrane, but the evaporation must proceed at least long enough to allow the collodion to set to a gel.

Brown (57) prepared a graded series of collodion sacs by allowing them to dry completely and then swelling them in alcohol–water mixtures of varying concentration. The higher the proportion of alcohol in the swelling solution, the higher the porosity of the resulting membrane, but the range of variation was limited, since a concentration of over 96 per cent of alcohol in the swelling solution would dissolve the collodion. The most highly porous membrane obtained was reported impermeable to filtration of Night blue and Congo red. Bendien and Snapper (40) used a similar procedure, incorporating small amounts of ether into the swelling solution.

Addition of various non-solvents or precipitating agents to a collodion solution was found to increase, to a limited degree, the porosity of membranes prepared from it; among these reagents were glycerol (250), water (224), lactic acid (86), and ethylene glycol (234). The porosity increase was limited by the effect on the strength of the membrane, which became fragile if too much reagent was added, and it was impossible to prepare membranes of high enough porosity for some bacteriological purposes. Asheshov (3), however, prepared membranes of high porosity by adding to the collodion solution a mixture of amyl alcohol and acetone.

Elford (93), as the result of a systematic study of the effect of many reagents on the porosity of membranes prepared from collodion solutions, found that in general addition of good solvents caused a decrease in membrane porosity, and non-solvents or precipitating agents an increase in porosity (cf. Pierce (234)). Amyl alcohol or acetone alone was a good solvent, but in the presence of each other there was an antagonistic effect which resulted in a porosity increase. On this basis, it was possible to compose mixtures of ether, ethyl alcohol, amyl alcohol, and acetone, to which were added small quantities of other reagents, for preparing a graded series of membranes of optimum mechanical properties and with porosities covering a very wide range (2 μ to 2 mμ). Porosities were increased in steps by addition of water or amyl alcohol, and decreased by addition of acetic acid or (107) ethylene glycol monoethyl ether (Cellosolve). Fine adjustments in porosity were made by altering the evaporation time. This permitted grading of porosity on a continuous scale.

The effect of various reagents on the porosity of Elford membranes is shown in figure 1, giving data (103) for membranes made from Necol (from Nobel Chemical Industries, Ltd.). The results of Bauer and Hughes (15) with Parlodion (du Pont) were entirely similar.

The results of adding various reagents to ether–alcohol collodion solutions, as influencing the membranes prepared from the latter, are summarized as follows: Ether–alcohol mixture (4), dilutes the collodion and makes membranes thinner, more porous, and rather brittle; ether (93), dilutes the collodion, making membranes thinner without much alteration in porosity; ethyl alcohol (93), makes membranes thicker and weaker, and decreases the porosity; methyl alcohol (93), decreases porosity; amyl alcohol (4, 93), decreases porosity, but, in the presence of acetone, increases the porosity; water (93, 224), increases porosity; if added in too great amounts, makes membranes brittle and non-uniform; acetic acid (86, 93), decreases porosity markedly; lactic acid (86), increases porosity; ethyl acetate (4), increases porosity markedly; ethyl formate (4), increases porosity; glycerol (86, 250), increases porosity; castor oil (250), increases porosity and toughness; ethylene glycol (234), increases porosity; Cellosolve (107), decreases porosity markedly.

C. STRUCTURE OF MEMBRANES

Some model of the structure of ultrafilter membranes must be assumed for the quantitative calculation of porosity from calibration data. The limited means for studying membrane structure experimentally must be employed in order to select the most suitable model.

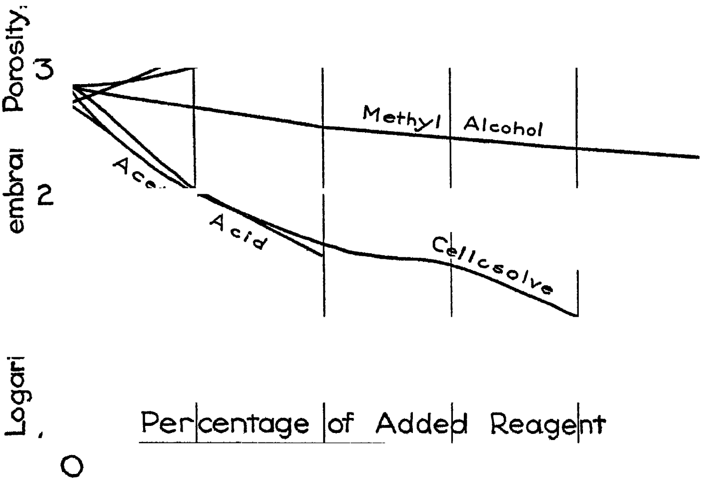

FIG. 1. Influence on membrane porosity of various reagents added to ether-alcohol collodion (Elford's parent amyl alcohol-acetone mixture). The logarithm of the porosity in mμ is plotted against the percentage of added reagent (93, 103).

1. *Models of membrane structure*

The most simple model of an ultrafilter is a sheet pierced by right circular cylinders, so that the effect in filtration is that of a bundle of cylindrical capillaries. This was the assumption made by Bechhold (18) in calibrating his acetic collodion membranes.

Manegold (201, 202) has discussed possible arrangements of porous structures in some detail, distinguishing between canal structures (pores, cracks) where the solid phase is continuous, and branching structures (packed spheres, packed parallelopipeds, packed rods, etc.) where it is not.

The latter type seems *a priori* the more likely in the case of a gel membrane, but it is much more difficult to treat. As for canal structures, Manegold specifies six arrangements:

(a) Pores (circular cross section), all running perpendicular to the membrane surface.
(b) Pores, a third of the total number running in each of three mutually perpendicular directions, without any intersections.
(c) Pores, oriented in haphazard directions, without any intersections.
(d) Cracks or slits (rectangular cross section), all running perpendicular to the membrane surface.
(e) Slits, a third of the total number running in each of three mutually perpendicular directions, without any intersections.
(f) Slits, oriented in haphazard directions, without any intersections.

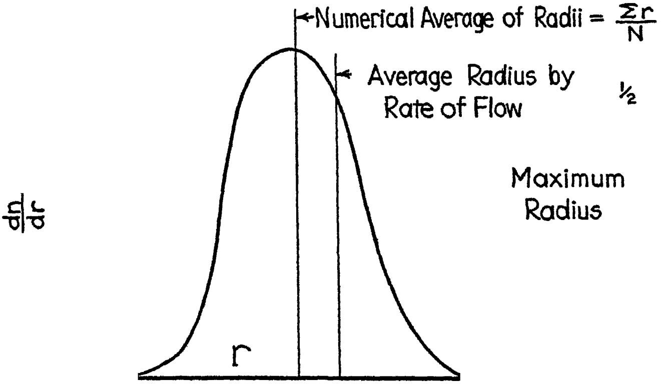

FIG. 2. Schematic distribution curve of pore sizes

As far as rate of flow of water through the membrane is concerned, it is impossible to distinguish between any of these structures. Manegold, after varied experimental studies on ether–alcohol membranes, concluded that structure (f) is the most likely. This was not, however, the only interpretation of his data possible (see below). Most evidence points to structure (a), with slight modifications, as a satisfactory working basis.

As an example of a structure with non-continuous solid medium may be cited the model of closely-packed spheres discussed by Tinker (272). In the case of collodion membranes, this structure is eliminated because it does not provide a large enough proportion of free space (see below; cf. Manegold, Hofmann, and Solf (206)).

Perhaps even more important than the shape and orientation of the interstices of an ultrafilter is the degree of uniformity of their dimensions. This may be represented by a distribution function; thus, if structure (a) is adopted, the quantity

$$\frac{1}{N} \cdot \frac{dn}{dr}$$

is plotted against r (figure 2), where N is the total number of pores, and dn is the number whose radii lie between r and $r + dr$.

2. Experimental study of structures

a. Microscopical studies. Elford (92) employed films from acetic collodion and ether–alcohol collodion, prepared under various conditions, for studies with the microscope and ultramicroscope. Two types of structure were distinguished. The *microgel* structure has interstices of microscopic dimensions, and is highly irregular, offering pores of different diameters. This type of gel is formed when membranes are prepared from dilute acetic collodion coagulated in water, or ether–alcohol collodion which is coagulated in water before the evaporation has proceeded long enough to set the film to a gel. It results from diffusion of water, a precipitating agent, into the collodion solution while the latter is fluid and the micelles are mobile. On the other hand, the *ultragel* has a very fine, uniform, granular structure, revealed only by the ultramicroscope. This gel is formed when ether–alcohol collodion is allowed to "set" before immersion in water, or when films of acetic collodion of high viscosity or extreme thinness are treated with water. It results from the replacement of solvent by water in a structure which is largely immobile while the replacement proceeds, the collodion micelles being held fast in a previously set gel, or oriented by surface forces in a very thin film, or behaving as if immobile in a solution of high viscosity. In ether–alcohol collodion membranes, which are in practice prepared by immersing in water only after the gel has set, the ultragel structure prevails. In acetic collodion membranes, the structure grades between microgel and ultragel according to the viscosity of the impregnating solution and the thickness of the impregnated film. This explains the lack of uniform porosity in the latter membranes. The ultragel structure is the desirable one; unfortunately the ultramicroscope can give no information concerning its geometrical details.

b. The specific water content. One of the earliest methods of characterizing a membrane was by the proportion of empty space in its structure (279). In practice, the "specific water content" is defined (102) as the relative loss of weight by removal of water from the filter pores, and this is identified with the total volume of all the pores.

The specific water content of ether–alcohol collodion membranes is remarkably high and constant for porosities from 20 mμ to over 1 μ, as shown by figure 3, which gives data for over two hundred Elford membranes (102). Entirely similar results were given by Manegold and Hofmann (203) for their membranes of pore diameters from 25 mμ to 60 mμ. The proportion of free space averages about 0.87 and is never less than 0.80 for all these membranes. Very close packing of pores in structure (a) would be required to provide this free space; hexagonal close packing, which gives a maximum of 0.905 for the circular cylinders in tangential contact, would barely suffice. Structures (b), (c), (e), and (f) are impossible for lack of room for non-intersecting pores. If pores are to be postulated running in three mutually perpendicular directions, they must be considered to intersect to an extent dependent on the value of the specific water content (102).

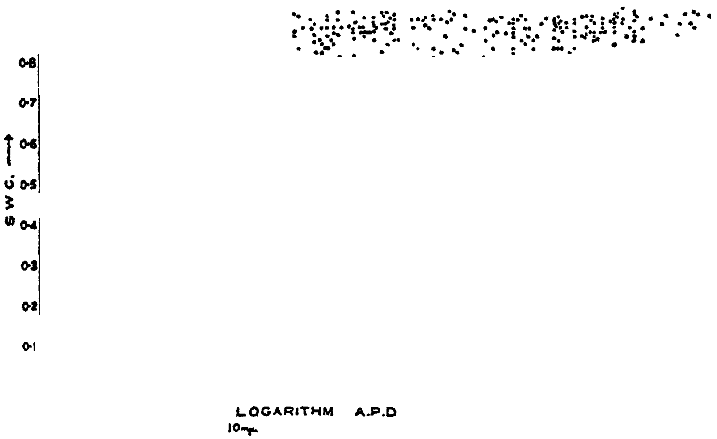

FIG. 3. The specific water content of Elford membranes, plotted against the logarithm of the porosity in mμ (102)

c. Rates of flow and average pore diameter. Estimation of the porosity of a membrane by measurement of the rate of flow of water through it was first suggested by Guérout (146) in 1872. The rate of flow through membranes, as a means of characterizing them, was applied by various workers, who studied its dependence on experimental conditions. It was found to be proportional to the pressure for Pfeffer's copper ferrocyanide membranes (233) and for ether–alcohol collodion membranes (45, 45b, 83, 203), demonstrating that the flow is viscous. However, deviations from the proportionality law have been observed in both directions; the increase in rate of flow with increasing pressure may be greater than linear (203, 176a), which is attributed to distortion of the membrane at high pressures, or to bringing immobile surface layers of water into motion at high pressures; or it may be less than linear (76), which is attributed to restriction of the area through which flow occurs when the membrane is forced against a perforated support at high pressures. This last effect shows that when rate of flow measurements are made for the purpose of porosity calculations, the membrane must not be supported against a wire gauze or perforated plate, since the calculations require accurate definition of the area through which flow is occurring. In the case of a mechanical support, the area effective in filtration varies from the total area of membrane, at low pressures (76), to the limited area actually opposite the perforations, at high pressures (95). When the effective area is clearly defined, and the pressures employed do not distort the membrane, the rate of flow is almost strictly proportional to the pressure. The dependence of rate of flow on temperature has been found for collodion membranes to be non-linear, and may be entirely attributed to the temperature variation of the viscosity of the flowing liquid (83). Above 75°C., however, this relationship no longer holds, since the membrane structure itself becomes altered and shrinks (76). The reproducibility and independence of time of the rate of flow of water, so long as blocking of pores by foreign particles or molds is eliminated, has been shown by Manegold and Hofmann (203). Cox and Hyde (76) showed that the rate of flow of water through collodion membranes was independent of pH from pH 1 to 12. Solutions of higher alkalinity attacked the nitrocellulose.

Calculation of the absolute porosity of a membrane from rate of flow measurements is made on the basis of three assumptions:

(1) The water flows through parallel cylindrical capillaries of circular cross section (structure (a) of page 387).

(2) The rate of flow of water is governed by Poiseuille's law.

(3) The total volume of pores, as given by the specific water content, represents the total volume effective in filtration; i.e., (*a*) there are no "blind" channels or pores which do not open on the surface; (*b*) there is no appreciable immobilized layer of water lining the pore walls.

In this case, the rate of flow is given by the expression

$$\frac{V}{t} = \sum_{i}^{N_A} \frac{\pi r_i^4 P}{8\eta l} \tag{1}$$

where V is the volume passing in time t, N_A is the number of pores opening on a surface area A, r is the radius of the i^{th} pore, P is the pressure producing flow, η the viscosity of water, and l the capillary length,—set equal to the thickness of the membrane. Now, by assumption 3, the specific water content is given by

$$S = \frac{\sum_{i}^{N_A} \pi r_i^2 l}{Al} = \frac{\sum_{i}^{N_A} \pi r_i^2}{A} \tag{2}$$

and combination of this expression with expression 1 gives

$$\left(\frac{\Sigma r^4}{\Sigma r^2}\right)^{1/2} = 2\left(\frac{2V\eta l}{SAPt}\right)^{1/2} \tag{3}$$

The quantity on the left is obviously an average pore radius ($\bar{r}$) as determined by rate of flow. This type of average weights the larger pores more than does a numerical average (figure 2). The "porosity" of membranes is more frequently referred to by the average pore diameter, j:

$$j = 2\bar{r} = 4\left(\frac{2V\eta l}{SAPt}\right)^{1/2} \tag{4}$$

The extent to which the above assumptions are justified, and the effects of their invalidity on the significance of calculated values of j, are now examined. The consideration is confined to ether–alcohol collodion membranes, and is particularly applicable to those of Elford.

Assumption 1, that of Manegold's structure (a), is the most arbitrary. In support of this assumption, it has been shown that a hexagonal close-packing of cylindrical capillaries will account for the observed water contents of membranes of porosities from 20 mμ to 2 μ; and it is difficult to picture any other structure which would do so and still provide the mechanical strength possessed by these membranes. The hexagonal arrangement is further suggested by the fact that a macroscopic pattern of hexagons and six-pointed stars is formed on the surface of the more porous ether–alcohol collodion membranes during evaporation. It is likely that this pattern is repeated on smaller scales within the visible hexagons, the pores themselves being ultimately formed by such an arrangement. This is supported by Elford's observation (102) that the collodion particles constituting the ultragel tend to link up forming chains and closed rings. The result is probably a structure resembling a honeycomb. Bartell and Van Loo (12a) suggest that, during evaporation, vortices are formed, the elementary unit being a hexagonal cell in which the evaporating solvents stream upward in the center and radiate to the edges. Altogether, a hexagonal arrangement of pore openings in the membrane surface seems probable. It does not follow, however, that the pores run straight and perpendicular to the surface. A honeycomb structure may involve a lateral "staggering" of the constituent nitrocellulose particles, resulting in a certain degree of tortuosity in the pores. This would necessitate, however, an intercommunicating system, and, for the membranes of high water content, Elford and Ferry suggest that the effective pore length or path of flowing water is probably less than twice the membrane thickness (102), this being supported by data for free diffusion through membranes (see below), although Bechhold believes it to be three or four times the membrane thickness (25).

But for membranes of porosity below 20 mμ, where the water content is lower and non-intercommunicating tortuosities are permissible, the channels may be considerably prolonged, so that substitution of the membrane thickness for l in equation 4 makes the calculated value of pore diameter come out too small.

The general validity of assumption 2 is shown by the work of Duclaux and Errera (83), who found rates of flow of water, solutions, and organic liquids through collodion membranes to be inversely proportional to the viscosities of the flowing systems, and proportional to the pressures employed. Poiseuille's law may be invalidated, however, by electrokinetic effects, or by steric effects for pores so small that the water cannot be considered as a continuous medium. These complications, which should be expected for pores less than 10 mμ (94), would make the flow less than that demanded by Poiseuille's law, and make the calculation of average pore diameter by equation 4 come out again too small.

Assumption 3a depends on the absence of cavities in the membrane which are ineffective in transmitting flowing water. It would, therefore, not hold for structures (b) and (c) of Manegold, where the pores are assumed non-intersecting. For either of these structures, the average pore diameter as calculated by equation 4 is too small by a factor of 0.58 (47). However, for a membrane of specific water content of 0.87, intersection is a geometrical necessity, and for pores equally distributed in three mutually perpendicular directions the error introduced by assumption 3a is much less, the factor being 0.75 (102). For the actual membrane, even this is probably an overestimate of the deviation, the factor being more likely still closer to unity, because the membrane, prepared in the form of a thin film with processes like that suggested by Bartell and Van Loo in progress, is not apt to possess an isotropic structure with pores distributed evenly in various directions. Marked orientation should be favored, resulting in preference for channels perpendicular to the surface. On the other hand, for membranes of porosity below 20 mμ, with lower water contents, the possibility of blind channels and even completely isolated sacs arises; the effect of using S in equation 4, instead of a smaller value representing the fraction of volume actually effective in filtration, is again to make j come out too small.

Invalidity of assumption 3b also makes the calculated average pore diameter too small. The magnitude of the effect depends on the ratio of the thickness of the layer of immobilized water to the radius of the pore; it is probably negligible for porosities above 100 mμ (since such membranes can be dried and re-wet reversibly), and below 100 mμ becomes of increasing importance with decreasing porosity.

Elford and Ferry (102) concluded that the effects of all these factors represent an error in the average pore diameter of not more than 25 per cent, when equation 4 is applied to membranes of porosities greater than 20 mμ.

d. Dialysis, diffusion, and conductivity. When a solute diffuses through a membrane, if there are no specific steric influences (the diffusion is free), the only effect of the membrane is to reduce the area through which the diffusion takes place,[5] and (if the length of the pores is greater than the membrane thickness) to reduce the gradient of concentration. Thus,

$$K' = \frac{K\delta\Sigma q_i}{Al} \tag{5}$$

where δ is the membrane thickness, q_i is the area of the i^{th} pore opening on the top surface, l is the pore length, K the free diffusion constant, and K' the apparent diffusion constant for diffusion through an area of membrane A corresponding to the summation Σq_i. The ratio $\Sigma q_i/l$ may thus be calculated from experimental values of K and K'. The quantity $\delta\Sigma q_i/AlS$ is a pure number which should theoretically be unity for membrane structure (a)—pores all perpendicular to the top surface—and should have the value of $\frac{2}{3}$ for structure (f)—slits haphazardly oriented. Measurements by Manegold (201) permit the calculation of values of $\delta\Sigma q_i/AlS$ for hydrochloric acid, urea, and sucrose. Above an average pore diameter[6] of 35 mμ, these values were independent of the porosity, being 0.64, 0.72, and 0.80 respectively. Below 35 mμ, they decreased with decreasing porosity. Similar results had been noted by Oldenburg (227) for diffusion of sodium and potassium chlorides. The numerical values of $\delta\Sigma q_i/AlS$ for high porosities were interpreted by Manegold as evidence for structure (f) for membranes of porosity over 35 mμ. In view of the preceding discussion, however, structure (f) being actually a geometrical impossibility, an alternative explanation seems more likely. This is that the interstices are pores, not slits, and that there is enough tortuosity in them to decrease the ratio δ/l somewhat below unity, and that a small fraction of them do not open on the top surface, making the ratio $\Sigma q_i/AS$ accordingly less than unity; so that the product, $\delta\Sigma q_i/AlS$, is as low as 0.64 to 0.80. The decrease in the product with decreasing porosity is at first attributable to a change in membrane structure, with increasing tortuosity of pores and an increase in the proportion of pores which do not open on the top surface,—effects already suggested by the decrease in the water content for porosities below 20 mμ. That the diffusion is at first still "free," so that equation 5 is applicable, is indicated by the fact that hydrochloric acid and sucrose filter in undiminished concentration through membranes of porosity as low as 15 mμ (204), probably as low as 5 mμ (96), and by the fact that a Ladenburg correction for viscous drag, as used by Friedman and Kraemer (128), is capable of accounting for only a small part of the decrease in diffusion with decreasing porosity. At very low porosities, however—perhaps below 5 mμ—the Ladenburg correction, electrostatic and electrokinetic effects (in the case of an electrolyte), and other factors enter to a degree which invalidates equation 5. The ratio K'/K decreases more rapidly and becomes zero at a porosity representing complete impermeability to the diffusing solute.

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[5] This reduction of the area through which diffusion occurs is called by Friedman and Kraemer (128) "mechanical blocking," a terminology which should be distinguished from the frequent use of "blocking" to signify progressive clogging of filter pores in the filtration of a disperse phase (part III).

[6] These porosities are in terms of average pore diameter on the basis of structure (a), recalculated from Manegold's data, which are usually expressed in terms of half slit widths on the basis of structure (f).

Very similar considerations hold for conductivity measurements, provided the concentration of electrolyte used is sufficiently high that surface conductivity may be neglected. Manegold and Solf (207), using potassium chloride, showed that the ratio of the specific conductivity through a given membrane to the bulk specific conductivity decreased with increasing concentration, attaining constancy above 0.03 N, where surface conductivity became negligible. Measurements with 0.1 N potassium chloride provided values for $\delta\Sigma q_i/AlS$ of about $\frac{2}{3}$ for a porosity[6] of 40 mμ, decreasing to about $\frac{1}{3}$ for 13 mμ. Measurements by Hitchcock (153) gave somewhat higher values for the quotient, approaching unity for the more porous membranes. Manegold's conclusions of an irregular slit structure (f) to give a value of $\frac{2}{3}$, grading at lower porosities into an irregular pore structure (c), with possible inclusions of isolated sacs, to give a value of $\frac{1}{3}$, may be replaced by the postulate of a structure of pores of a slight tortuosity, the majority of which open on the top surface, the fraction which do not so open, and the degree of tortuosity, increasing with decreasing porosity below 40 mμ.

Michaelis (216) found that two solutions of potassium chloride in different concentrations, between which only a very slight diffusion potential should exist because of the equal mobilities of the two ions, did develop a diffusion potential when separated by a membrane of sufficiently low porosity. Manegold and Viets (208) and Elford and Ferry (103), studying the potential as a function of the membrane porosity, found it to be only very slight above a certain limiting porosity (average pore diameter about 3 mμ (103)), while below this porosity the potential rose sharply to its maximum theoretical value (57 mv. for a tenfold concentration difference). The limiting porosity probably corresponds to the point where the chloride ion is excluded from pores by electrostatic repulsion (cf. part IV, A, 3).

e. Distributions of pore sizes. An indication of the distribution of pores in ultrafilters (cf. figure 2) was obtained by Bechhold (18) by application of Cantor's law (previously suggested by Barus (13) in 1894), as follows. If the opening of a circular capillary is wet with liquid, and a pressure P is required to force through a non-wetting fluid immiscible with the first, then the diameter of the opening is given by

$$d = \frac{4\gamma}{P} \tag{6}$$

where γ is the surface tension of the interface between the two fluids.

If air is forced through a wetted membrane in this way, visual observation of the increase in frequency of bubbling as the air pressure is increased gives a rough measure of the distribution of the largest pores. The pressure at which the bubbling begins determines the maximum pore size, and the ratio of this to the average pore size as determined by rate of flow is an indication of the degree of isoporosity or heteroporosity. For acetic collodion membranes, this ratio is from 5 to 10; for Elford membranes, it is as low as 2, showing these membranes to be relatively isoporous.

The same principle may be applied to forcing a foreign liquid, such as isobutyl alcohol, through a membrane wet with water (33). In this case, much lower pressures are required, since the surface tension is lower. It must be noted, however, that the minute droplets of the foreign liquid which are forced through the pores are invisible until they coalesce to form larger drops, and this takes time (34). For validity of equation 6, the contact angle of the liquid–liquid interface with the pore wall must be 0°. This question has been examined by Erbe (113). The condition for zero contact angle is that a layer of the original liquid remain lining the pores after the second liquid has been forced through, i.e., the original liquid must wet the membrane the better. For cellulose (cellophane and Cella filters) the original liquid should be water, through which isobutyl alcohol is forced. The fact that the pores are still lined with water at this point is indicated by the rate of flow value for the alcohol being too small (after taking into account the difference in viscosity). For nitrocellulose, on the other hand, the isobutyl alcohol wets the better and should serve as the saturating liquid, water being forced through as the second liquid. In this case, the experiment may not be prolonged, or the water will displace from the pore walls the lining of alcohol, giving a contact angle no longer zero. Saturated solutions of the two liquids in each other behave in wetting practically the same as the respective pure liquids.

Combination of the bubble pressure and rate of flow methods gives the Bechhold–Karplus procedure (114) of determining the whole distribution curve schematically illustrated in figure 2. The rate of flow of water through a nitrocellulose membrane wet with isobutyl alcohol (or *vice versa* for cellulose or an animal membrane) is determined as a function of pressure. At any given pressure, the observed flow represents the total occurring through all pores large enough to pass the non-wetting liquid at that pressure. The curve of flow as a function of pressure is shown in figure 4. From this, by breaking it up into fictitious discontinuities, may be calculated the distribution of pore radii (figure 5a), the distribution of pore areas (figure 5b), and the distribution of flow (figure 5c).

Pisa (235) employed this method to test several types of membranes. Cella filters were far from uniform, the ratio of maximum to minimum pore diameter ranging from 3 to 5, and two pieces from the same membrane differing considerably in distribution curves and in average pore diameter (also checked by filtration of hemoglobin). Few data were quoted for acetic collodion membranes; in one case there was a sixfold range of pore sizes without a marked maximum in the center of the distribution curve. Among natural membranes, chorion from sheep was found to be quite isoporous, but variable from piece to piece, while amnion was exceptionally isoporous.

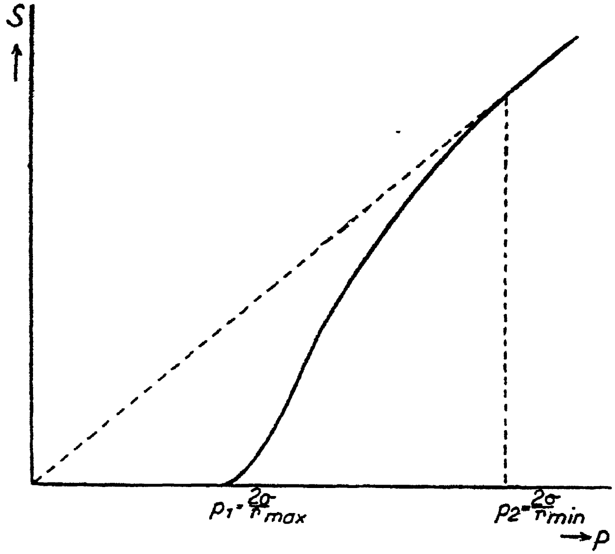

FIG. 4. Flow–pressure curve for the Bechhold–Karplus experiment (114)

A good test for isoporosity is given in filtration experiments with a monodisperse system, especially with a biological material which is detectable in very minute quantities. The porosity ratio of the smallest-pored filter which passes the disperse phase in undiminished concentration to the

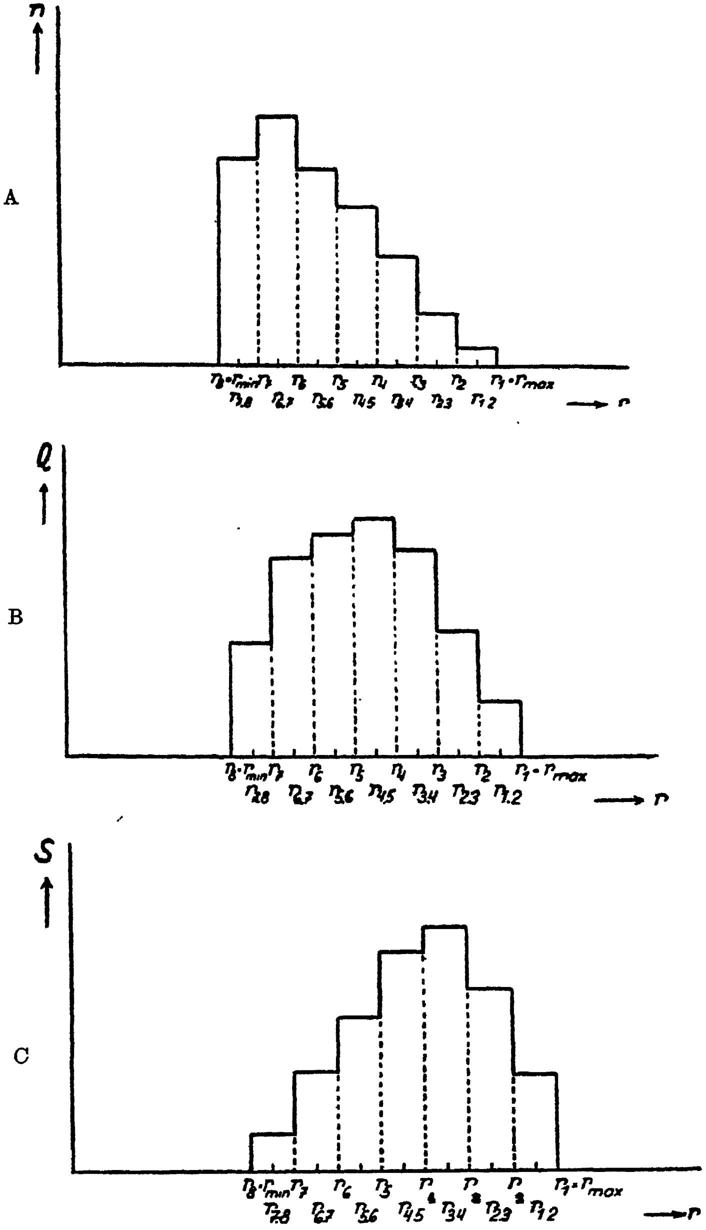

FIG. 5. Distribution curves determined by the Bechhold–Karplus procedure (114). (a) Distribution of pore radii; (b) distribution of pore areas; (c) distribution of flow through individual pores.

largest-pored filter which retains it completely is a measure of the pore uniformity. For filtration of viruses and bacteriophages by Elford membranes, this ratio is seldom greater than 2, a value approximating that anticipated on statistical grounds for a filter of perfect isoporosity (cf. part III, F).

3. Mechanism of variation of porosity

It is remarkable that membranes of collodion may be prepared covering a porosity range of a thousand fold, and particularly that in the greater part of this range ($j = 2\mu$ to $j = 20$ mμ) the total space occupied by the pores is independent of the size of the latter. Increase in porosity is evidently accomplished by redistribution of the nitrocellulose particles so that the pores become larger but also less numerous. This is probably a result of a reversible, gradual aggregation of the nitrocellulose, giving progressively larger particles (102)—particles which are not spherical, but elongated, as shown by streaming double refraction (256). Such gradual aggregation is exceptionally favored by a solvent containing amyl alcohol and acetone, explaining how the method of Elford can give such highly porous membranes with uniformity and adequate tensile strength. Presence of water favors aggregation, but it is not gradual; it produces flocking and coagulation, and the resulting membrane may be fragile and non-uniform. The difference between the action of water and that of amyl alcohol and acetone is clearly shown by titrating collodion solutions with these reagents (107).

The preparation of an ether–alcohol collodion membrane consists essentially in the evaporation of solvents until the film sets to a gel. The degree of aggregation of collodion at any point in the process depends in a highly specific manner on the composition of the solution. The composition of the solution depends in turn on the time elapsed and on the original proportions and volatilities of the various solvents and non-solvents in the solution. Two processes probably occur during the evaporation (107): a gradual aggregation as the proportions of solvents and non-solvents change, and a sudden gelling when the concentration of collodion becomes sufficiently high for the aggregates to lock into a rigid structure. The extent to which the aggregation has proceeded by the time gelation occurs determines, largely, the membrane porosity. Further evaporation from the set gel, accompanied by shrinkage of the gel when it is immersed in water, will decrease the eventual porosity.

D. CALIBRATION OF MEMBRANES

1. Significance of calibration

There are two fundamental questions in characterizing an ultrafilter. One concerns its average pore size and distribution of sizes; the other, its behavior in filtering particulate systems. The first question is answered by measurements of specific water content, rates of flow, and bubble pressures. The second involves consideration of the complex mechanism of filtration (part III). The second question is the more important in the study of ultrafiltration, as distinguished from that of the membranes themselves, but it is not convenient to characterize ultrafilters in terms of filtration of disperse systems alone. In the first place, the behavior of a filter toward one sol may differ from its behavior toward another of similar particle size. In the second place, characterization by filtration of particles of known size does not provide a continuous scale of grading. Given an ultrafilter, it is hardly possible to command a wide series of sols of different particle sizes so closely spaced as to permit selecting one which the filter retains and another, only slightly finer, which the filter passes. On the other hand, calibration by rate of flow of water assigns a specific average pore diameter to the filter. Values of average pore diameter, as calculated by equation 4, provide a continuous scale, and, for ether–alcohol collodion membranes, are close to representing the true dimensions of the pores (probably within 25 per cent, for porosities above 20 mμ). The relationship between the diameter of a particle and the average pore diameter of the most highly porous filter which retains it is of a specific nature (part III).

2. Procedure of calibration

Calculation of the average pore diameter requires measurement of the membrane thickness, the specific water content, and the rate of flow of water through the membrane. In the convenient procedure of Elford (93) and Elford and Ferry (102), a uniform membrane sheet is cut into about forty discs, of which five or six are employed in measuring the above quantities, the remainder being subsequently available for filtration experiments.

a. Measurement of thickness. The membrane thickness is measured either by a micrometer gauge controlled by a fine spring, with precaution that the membrane is not compressed nor deformed, or by cutting a thin strip of membrane, bending it in the form of a Z to stand on edge, and observing it microscopically with a micrometer ocular. More refined methods may employ an optical lever (161) or even interferometry.

b. Specific water content. The specific water content, S, may be determined in three ways:

(a) By the difference in weights of the membrane with its pores full of water (W_w) and then dried by heating to 60°C. or over sulfuric acid (W_d):

$$S = \frac{W_w - W_d}{\delta A} \tag{7}$$

where δ is the membrane thickness and A the area.

(b) By consideration of the density of solid collodion, ρ; then

$$S = 1 - \frac{W_d}{\delta A \rho} \tag{8}$$

(c) (Acetic collodion membranes only) by assumption that the coagulation does not change the specific volume of the collodion, so that S equals the percentage of acetic acid in the impregnating solution.

c. Rate of flow of water. For a convenient measure of the rate of flow of water, Elford defined an auxiliary quantity, the "R.F.W." (F), in terms which lead to the formulation

$$F = \frac{V\delta}{AtP} \times 60{,}000 \tag{9}$$

where δ is the membrane thickness in millimeters, V is the volume of water which flows through an area A of the membrane in time t under a pressure P (in centimeters of water). Manegold and Hofmann (203) used a similar quantity (expressed in absolute units) for characterizing membranes. For the range of Elford membranes, F varies 10^6-fold, so that apparatus must permit measurement of large and small volumes of water and application of low and high pressures. For the highest porosities a pressure of 10 cm. of water is sufficient; it can be safely increased to 350 cm. of water for the densest membranes. The membrane must be clamped securely to obviate leaks, but damage of the edge must be avoided. The area through which flow occurs must be clearly defined, thus precluding a support of wire gauze or perforated plate behind the membrane. The membrane consequently bulges when pressure is applied, and the resulting displacement of water in the apparatus must be controlled. Apparatus suitable for rate of flow measurements has been described by Brukner (60), Elford (93), Elford and Ferry (102), and Bauer and Hughes (15).

The average pore diameter may be calculated from F (at 20°C.) and S, after introduction of dimensional constants, by the simple expression

$$j \text{ (in microns)} = 0.234 \sqrt{\frac{F}{S}} \tag{10}$$

E. APPARATUS FOR ULTRAFILTRATION

Apparatus for ultrafiltration requires a water-tight clamp for the ultrafilter, with a vessel for the filtering system under pressure and a receiver for the filtrate (often under negative pressure). For specific cases, there are many individual features of the apparatus to be considered.

1. Construction of vessel under pressure

For high pressures the ultrafilter vessel must be constructed of metal. Stainless steel (125) and brass plated with nickel (10, 1) and silver (100) have been employed. For corrosive solutions glass is better, and it has the further advantage of transparency. Grabar (141) has described a filter in which the solution and filtrate need touch nothing but glass and membrane at any point. For filtration of bacteriological systems, the apparatus must be sterilizable and there must be no exposure of metals which have toxic effects. In sacs and filters of the Bechhold-König type, the filter forms its own vessel, which is closed at the top by a rubber stopper sealed with collodion or the like, or left open to the atmosphere for filtration under negative pressure.

2. Support of membrane

The filter membrane may be supported on a perforated metal plate (130, 10) or metal tube (126), a fine wire gauze (61, 190), or a sheet of perforated glazed porcelain (293). Filter paper may be interspersed between the membrane and the rigid support, in an effort to increase the area effective in filtration. The latter is always, however, considerably reduced by a perforated support. The fact that filtration under a substantial pressure (2 atmospheres) takes place only opposite the perforations was shown by experiments of Elford in filtration of hemoglobin (95). A disc of sintered Jena glass (141) forms an admirable support in making use of the entire membrane area, but has the disadvantage of retaining a quantity of filtrate.

3. Gaskets

The filter may be sealed by gaskets of rubber (the customary material) or, where this is objectionable, of heavy swollen cellophane (195).

4. Clamping

A circular threaded ring is recommended for clamping, as giving even pressure all around the periphery of the membrane. It should be designed to prevent any shearing of the membrane (10). For higher pressures, where this does not give a tight seal, a series of individual bolts arranged around the periphery is employed (61).

5. Pressures applied

Filtration under negative pressures is not recommended for quantitative work, since the filtrate tends to concentrate by rapid evaporation (7). Further, it is difficult to collect successive samples of filtrate, a procedure necessary for adequate analysis of results. It is convenient, however, for filtration of large volumes of material through highly porous filters, where the upper vessel may be often replenished. For filtration through membranes of low porosity, very high positive pressures may be desired. The designs of the Göttingen Commercial Filters (188), of Brukner and Overbeck (61, 62), and of Folley and Mattick (125) permit pressures up to 100 atmospheres.

6. *Stirring*

Bechhold (16) showed that ultrafiltration was often favored and expedited by stirring. He employed a mechanical stirrer with a shaft which emerged from the upper vessel through packing. The apparatus of the Göttingen Filters (188) and of Brukner and Overbeck (61) is equipped with a magnetic stirrer operated from the outside by a rotating electromagnet. Kronsbein (168) devised a reciprocating stirrer for thorough agitation in a filter cell in which the membrane was held vertically.

7. *Filtration of small volumes*

Apparatus designed especially for filtration of small volumes of material includes the arrangements of Augsberger (7), who employed an inverted Giemsa tube (137) with positive pressure, and de Waard (277) and Tóth (273), who ultrafiltered in a centrifuge, the centrifugal force replacing pressure. The design of Tóth, however, involved a membrane of the Bechhold–König type, which is itself unsuited for filtering small volumes, because of the retention of filtrate.

8. *Miscellaneous*

Other ultrafiltration apparatus has been described by Walpole (280), Malfitano and Michel (200), Fouard (126), Smith (259), Spiegler (262), Aitken (1), Breedis (52), Zakarias (291), Wilenskii (286), and Thiessen (270).

III. THE MECHANISM OF ULTRAFILTRATION OF DISPERSE SYSTEMS

When a disperse system is forced through an ultrafilter, the disperse phase may be less concentrated in the filtrate because it is (a) adsorbed on the surface of the filter and its pores (primary adsorption), (b) retained within the pores or excluded from such blocked pores (blocking), or (c) mechanically retained on top of the filter (sieving). The latter sieve action may result from heterodispersion in the filtered system or heteroporosity in the filter, or from purely statistical effects (compare section F). The principal problem in selecting conditions for carrying out ultrafiltrations is to eliminate effects a and b as completely as possible, so that sieving, the desired effect, is the controlling factor. The operation of these three mechanisms may change with time as the filtration proceeds, so that, in the first place, examination of the course of filtration throws light upon the problem.

A. EXPERIMENTAL PROCEDURE

The ideal method for following an ultrafiltration experiment would involve continuous measurement of concentration of filtrate and residue during the whole process, without necessitating withdrawal of samples. This is possible in some cases by measurement of refraction or light absorption (208), but imposes serious limitations on the filtration apparatus. It is almost always possible, however, to separate the filtrate into successive small samples for individual analysis, and to withdraw small samples from the residue from time to time if desired. Whenever feasible, a physical analytical method is preferable; refractometry has been successfully used (188, 94, 193), as well as colorimetry (94) and conductivity (195, 89) and surface tension (89). For biological systems, immunological reactions or animal tests are usually required.

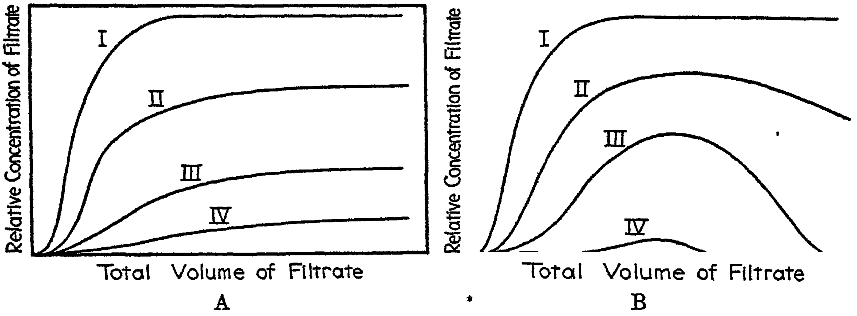

FIG. 6. Typical filtration curves. (a) Normal filtration; (b) abnormal filtration

The relative concentration of filtrate is defined as the ratio of the concentration of a momentary small sample of filtrate to that of the original solution. When this is followed through the course of a filtration, a curve of one of the forms shown in figures 6a and 6b results. Curves I arise from filtration through membranes whose pores are far wider than the solute particles. When the pore sizes are of the same order of magnitude as the particle sizes, the curves may take the form of either II-IV in figure 6a (100), or II-IV in figure 6b (100, 235). In every case, the initially low values of filtrate concentration are attributed to a primary adsorption of the solute in the membrane pores; this becomes satisfied as soon as a sufficient volume has been filtered through (depending, of course, on the concentration of the filtering solution). After this, the solute or disperse phase appears in the filtrate in practically undiminished concentration (curves I); or, if the pores are not large enough to permit this, the filtrate concentration levels off or slowly increases (figure 6a), attributed to sieve action; or reaches a maximum and falls off more or less rapidly (figure 6b), attributed to blocking.

The change with time of the concentration of the residual solution above the filter is also characteristic. When the solute appears in the filtrate in practically undiminished concentration (curves I), the concentration of the residue is also practically unchanged. True sieve action (figure 6a) is accompanied by an increase in the concentration of the residue, which may be many fold if the proportion of solute passing the filter is small and a large fraction of the original volume is filtered. Blocking (figure 6b) is accompanied by an increase in the concentration of the residue to some extent, but (unless it is occasioned by foreign particles) it always involves colloidal instability of the disperse phase and a tendency to flocculation and precipitation, so that the latter processes often occur in the residual solution, and the disperse phase, instead of concentrating, is precipitated on the membrane. Finally, in the case of marked primary adsorption from a limited quantity of a dilute solution, the concentration of the residue may be considerably diminished.

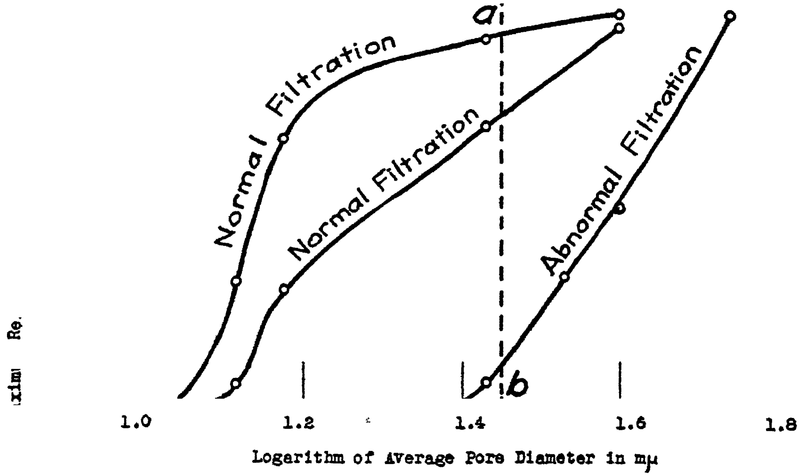

FIG. 7. End-point curves for filtration of serum albumin (100). The maximum relative concentration of filtrate is plotted against the logarithm of average pore diameter in mμ.

To obtain a quantitative measure of filterability of a given disperse system, equal volumes of the latter (volumes several times that required to satisfy primary adsorption) are filtered through membranes of different porosities. The maximum relative concentration of filtrate obtained in each experiment is plotted against the membrane porosity (semilogarithmically, for convenience), and curves of the type shown in figure 7 result. The intersection of such an "end-point curve" with the porosity axis determines the end-point porosity, i.e., the highest porosity which completely retains the disperse phase.

By adjusting experimental conditions, it is possible to isolate effectively the factors of adsorption and blocking, and to study means of their elimination.

B. PRIMARY ADSORPTION

Bechhold (16) pointed out the rôle of adsorption in removing the disperse phase from the ultrafiltrate, and advocated control experiments by shaking bits of membrane with the solution to be filtered, and thus determining the amount of adsorption. This procedure is not adequate, however, for complete interpretation of filtration mechanisms (94).

The effect of primary adsorption in filtration may be studied separately by employing filters with pores very much wider than the solute particles, so that no sieving nor blocking can occur; or by employing extremely dilute suspensions, as is possible in biological systems, so that a large volume is required to satisfy the adsorbing capacity of the membrane.

1. Influence of experimental conditions

a. Concentration of filtering solution. The more dilute the filtering solution, the greater the volume which must pass through the membrane before adsorption is satisfied and the disperse phase begins to appear in the filtrate. Elford's experiments with dyes (94) showed that, over a tenfold variation in initial concentration, the relationship was one of slightly less than inverse proportionality (figure 8). Similar results were found in the filtration of foot and mouth disease virus (129). Infective agents are always employed in very dilute suspension (see table 5); if limited volumes of filtrates from such a system are collected, it is clear that presence or absence of the agent in a filtrate will depend on the initial concentration. This is shown in figure 9 for *B. Prodigiosus* and vaccinia virus. Membranes of high porosity adsorb all the agent from a limited volume of low concentration. For a higher initial concentration, it is necessary to select a membrane of lower porosity—one which will introduce some sieve action—to retain the agent. Finally, for the highest concentrations, only membranes of porosities below the end-point value can retain the agent. This same effect was pointed out as early as 1910 by Steinhardt (263) in the filtration of diphtheria toxin and cobra venom through uncalibrated collodion sacs. It has been studied by Elford and collaborators for foot and mouth disease (129) and six different sizes of bacteriophages (98).

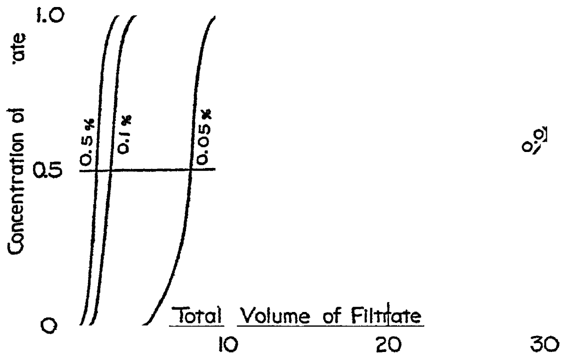

FIG. 8. Dependence of the zone of primary adsorption on concentration, for dilute solutions of dye (94). The numbers opposite the curves refer to initial concentrations of the filtering solutions.

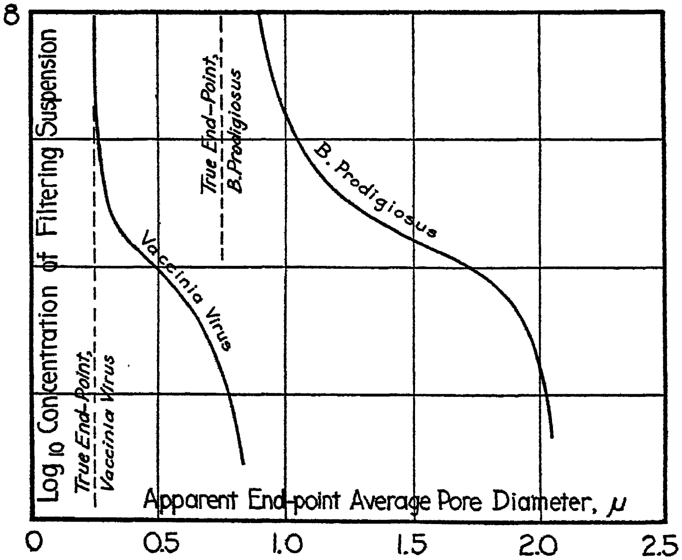

FIG. 9. Dependence of apparent end point on concentration for bacteriological systems, caused by primary adsorption (94)

b. Filtration pressure. Increase of pressure narrows the zone of primary adsorption, presumably by defining more closely against the filter support the areas through which flow can take place and by a tendency to shear away adsorbed layers in the pores. Figure 10 shows experiments by Elford (94) with the dye Night blue.

c. Thickness of membrane. The thicker the membrane the greater the adsorbing capacity, and accordingly the greater the volume which must be filtered before the disperse phase appears in the filtrate. This was pointed out by Steinhardt in experiments with cobra venom (263) and demonstrated by the results of Galloway and Elford with foot and mouth disease virus (figure 11) for membranes piled one on top of another.

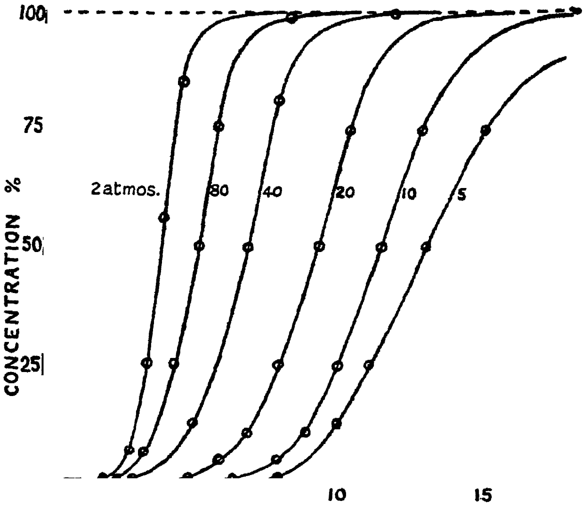

FIG. 10. Dependence of the zone of primary adsorption on pressure, for dilute solutions of Night blue (94). The relative concentration of filtrate is plotted against the total volume of filtrate. The numbers opposite the curves refer to pressures in centimeters of mercury, except the first, which is expressed in atmospheres.

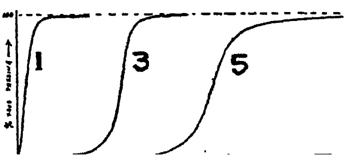

FIG. 11. Dependence of the zone of primary adsorption on membrane thickness, for foot and mouth disease virus (129). The figure opposite each curve indicates the number of membranes through which filtration took place.

d. Capillary-active substances. The presence of a capillary-active substance in the disperse system markedly decreases the zone of primary adsorption, as shown by the results of Elford on Night blue (figure 12), where saponin and sodium oleate are employed as capillary-active agents.

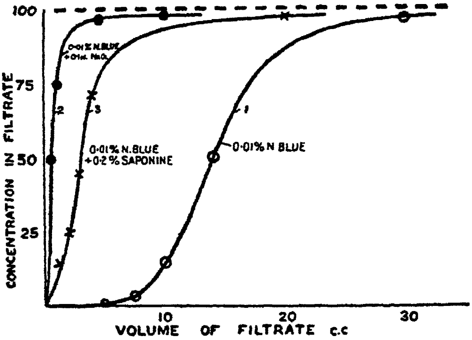

FIG. 12. Dependence of the zone of primary adsorption on the presence of capillary-active substances, for a dilute solution of Night blue (94)

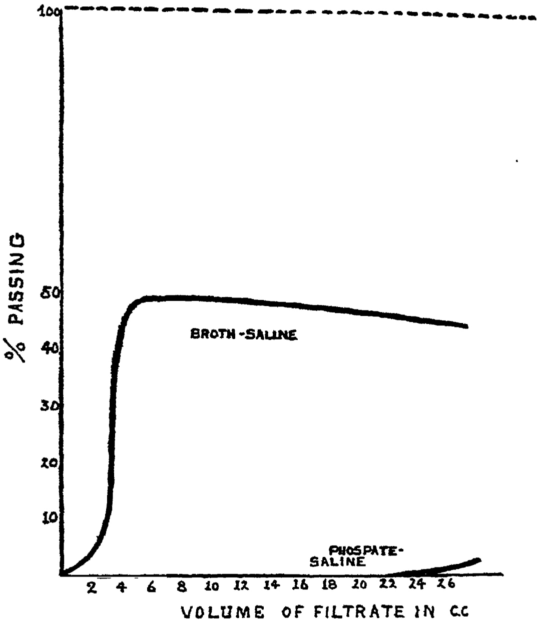

FIG. 13. Dependence of the zone of primary adsorption on the presence of a capillary-active substance, for foot and mouth disease virus (129)

The capillary activity of broth, as contrasted with phosphate-buffered saline, is shown by filtration of foot and mouth disease virus through collodion membranes (figure 13) and through Seitz filter candles (136). The effect is presumably due to preferential adsorption of the capillary-active agent (see part III, section D).

2. Suppression of primary adsorption

It is clear that the effect of primary adsorption can always be eventually eliminated by filtering a sufficient volume through the filter membrane. The adsorbing capacity is satisfied most quickly for (1) high initial concentrations of the filtering solution, (2) high filtration pressures, (3) thin membranes, and (4) presence of capillary-active substances.

C. BLOCKING

The effect of blocking may be studied separately by employing solutions of concentration sufficiently high to satisfy the primary adsorption at an early stage in the process. Blocking of ultrafilters is closely related to colloidal instability, and may be best studied in filtration of sols of a lyophobic tendency. Proteins near the isoelectric point offer convenient examples.

1. Influence of experimental conditions

a. Concentration of filtering solution. The more concentrated the filtering solution, the sooner blocking sets in, so that, under conditions of severe blocking, it is possible to find the maximum relative filtrate concentration related antibatically to the absolute initial concentration. This is the situation for serum albumin at pH 5.7 (figure 14).

b. Filtration pressure. Increase of pressure favors blocking. In particular, reduction of the applied pressure to zero—i.e., substituting dialysis for ultrafiltration—apparently eliminates the effects of blocking entirely (section G). Bechhold (19) found alternating periods of pressure and no pressure to be effective in filtering solutions of hemoglobin, while Elford (96) has employed an oscillating, reversing pressure to keep the filter pores cleared.

The effect of increased pressure on the filtration of a colloidal sol, favoring blocking and resulting in impaired filterability, is in contrast to the effect on the filtration of an emulsion, as found by Hatschek (148a) for solutions of lecithin. In this case, increase of pressure improves filterability, the droplets of the disperse phase being deformed and elongated and forced through pores too small to admit them in spherical form.

c. Membrane thickness. The thicker the membrane, the greater the ratio of pore length to pore diameter, and the more favorable are conditions for blocking. This has been demonstrated for filtration of serum pseudoglobulin near the isoelectric point (103).

d. Capillary-active substances. Presence of a capillary-active substance suppresses blocking (100), presumably by preferential adsorption with resultant "lubrication," enabling the particles to slip through the filter pores more readily (part III, D).

e. Foreign particles. Presence of foreign particles, larger than those of the principal disperse phase, may cause serious blocking of the pores by mechanical obstruction, even under conditions where the principal disperse phase itself does not tend to block because of colloidal instability. In fact, filtration of distilled water (rate of flow experiments) has been found to be impeded by blocking from dust particles unless the water is double-distilled or cleared by a preliminary filtration (113). When blocking is occasioned by foreign particles, accompanied by no flocculation of the disperse phase, the concentration of the residue should increase as in true sieve action.

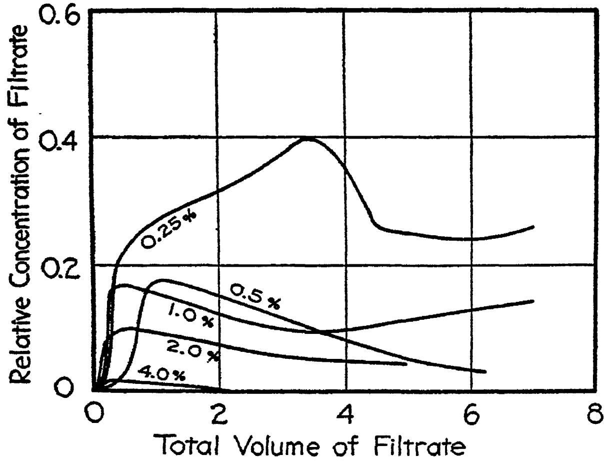

FIG. 14. Dependence of blocking on concentration, for serum albumin at pH 5.7 (100). The numbers opposite the curves refer to the initial concentrations of the filtering solutions.

2. Suppression of blocking

It is clear that the effect of blocking can be diminished by (1) low initial concentrations of the filtering solution, (2) low filtration pressure, (3) thin membranes, (4) the presence of capillary-active substances, and (5) absence of gross foreign particles.

D. CAPILLARY-ACTIVE SUBSTANCES

Conditions for suppression of adsorption and blocking agree in demanding the presence of a capillary-active substance, i.e., one which depresses the surface tension of the solution and is strongly adsorbed in interfaces, in particular, on the pore walls and on the surfaces of colloidal particles.

The effect of a protective colloid in facilitating filtration of lyophobic colloids was pointed out by Bechhold (16).

The first systematic study of the effect of capillary-active substances on membrane permeability was that of Brinkman and Szent-Györgyi in 1923 (53). They employed collodion sacs which were ordinarily impermeable to hemoglobin in ultrafiltration at 3 atmospheres pressure. Such a membrane became permeable to this protein when a dilute solution of sodium oleate was first passed through it. That the hemoglobin was unchanged was shown by filtration of the filtrate from a "soaped" membrane through an "unsoaped" one. The protein was retained by the latter in the usual manner. "Soaped" and "unsoaped" membranes had practically the same porosity, as shown by rate of flow of water, in spite of the difference in permeability to hemoglobin. Treatment of a soaped membrane with calcium chloride rendered it again impermeable. Other capillary-active substances could be substituted for sodium oleate with varying effectiveness,—sodium linolate, sodium glycocholate, digitonium, glycerol monooleinate, and Witte's peptone.

Clausen (72) prepared a capillary-active substance from urine of nephrosis by concentration, dialysis, desiccation, and extraction with alcohol. This substance, a wax, rendered permeable certain collodion membranes which were normally impermeable to protein,—an effect of physiological significance in view of the increased permeability of the kidney tissues to serum proteins in nephrosis.

The conflicting report of Norris (225) that the permeability of collodion membranes is unaltered by the capillary-active agents used by Brinkman and Szent-Györgyi and by Clausen, was really no contradiction to the work of the earlier authors. The results of Brinkman and Szent-Györgyi, who studied permeability to protein in ultrafiltration experiments, are ascribable to the suppression of blocking by the capillary-active agents. The data of Norris refer to permeability to calcium chloride in diffusion experiments; in this case no blocking would be expected in the absence of a capillary-active substance (section G), so that the addition of one would have no effect.

However, Faludi (118) reported that bile salts (of which sodium glycocholate is an example) do not influence the ultrafiltration velocity of serum or plasma when the former are employed at the concentrations occurring in the body. Bedson (39a) found that the permeability of collodion membranes to serum proteins in ultrafiltration was increased by a preliminary soaking in serum, and gave some evidence that the active agent in the serum was cholesterol. Tallerman (266) confirmed the effectiveness of serum, but not that of cholesterol. Nattan-Larrier et al. (223) found that collodion membranes normally impermeable to complement were made somewhat permeable by sodium oleate, taurocholate, or glycocholate, but not by egg albumin. It should be noted that the profound influence of pH on permeability to protein may overbalance that of a capillary-active agent (cf. part IV, C, 2). Rao (239) found that saponin increased the permeability of collodion, parchment, and various animal membranes to oxalic, lactic, and tartaric acids and sucrose in diffusion. The improvement in diffusion, considered as a function of the concentration of saponin, reached a maximum (rarely greater than 30 per cent) at a very small concentration. In the case of sucrose, a surplus of saponin even decreased the permeability. Amyl alcohol was also effective as a capillary-active agent.

Holman and Krock (156) made the remarkable observation that bacteriological candle filters became readily permeable to bacteria when "oiled" with paraffin wax or liquid paraffin. Oiled portions seemed to have larger pores as shown by the bubble test, but the rate of flow of water was decreased by oiling.

The effectiveness of bacteriological broth as a capillary-active agent was noted by Ward and Tang (281), who showed its influence on the permeability of filter candles to vaccinia and herpes viruses. The effect of Hartley's broth on the permeability of collodion membranes was studied by Galloway and Elford (129) in the filtration of foot and mouth disease virus and by Elford and Ferry (100, 101) in filtration of proteins at various pH values. This broth is ordinarily prepared from horseflesh by extraction and digestion with trypsin (148). The identity of the capillary-active substance in it is not known, except that it is destroyed by prolonged digestion with trypsin (100).

The mechanism of lubrication in filtration with a capillary-active substance is usually interpreted as a coating of the latter on both pore walls and particle surfaces. Evidence of such adsorption in fine-pored membranes has been found in rate of flow experiments by Grollman (145), Cox and Hyde (76), and Elford (96).

E. NORMAL AND ABNORMAL FILTRATION

While the conditions for suppression of primary adsorption and blocking agree in demanding thin membranes and the presence of a capillary-active substance, they disagree in their requirements for concentration and pressure. Optimum values of the latter must accordingly be chosen. For most infective biological systems, the optimum concentration is the highest concentration obtainable; for proteins, 0.5 per cent is satisfactory (100).

When blocking is effectively suppressed, so that the filtration curves have the forms of figure 6a, the filtration has been termed *normal* by Elford and Ferry (100). Filtration with blocking, giving curves like those of figure 6b, is *abnormal*. The latter is invariably associated with an abnormally high end point, so that filters impermeable to a given disperse phase under conditions of abnormal filtration may under normal filtration become permeable.

Occurrence of abnormal filtration apparently depends on the tendency of the particles of the disperse phase to aggregate and precipitate when they are crowded together, as when they are forced into the membrane pores. If the tendency to aggregation exists, multiple adsorbed layers will be built up within the pores, and pores ten times as wide as the particles may become completely blocked. Without this instability—i.e., when normal filtration obtains—the adsorption may be limited to a single layer, and, by selective adsorption of a capillary-active agent, even that may be suppressed (94). Schematic diagrams of these principles are shown in figure 15.

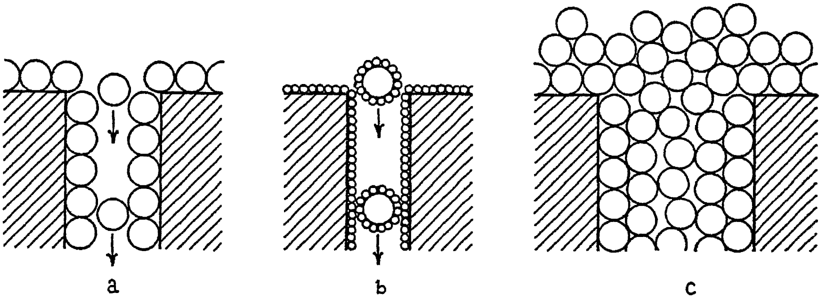

FIG. 15. Schematic representations of normal and abnormal filtration. (a) Normal filtration, in the absence of a capillary-active substance; (b) normal filtration, in the presence of a capillary-active agent; (c) abnormal filtration.

F. THEORY OF SIEVING

The desired mechanism for retaining the disperse phase in ultrafiltration is a mechanical sieving. The theoretical consequences of an idealized sieving operation are here considered.

1. Relationship of the sieve constant to the concentrations of filtrate and residue

Neglecting adsorption and blocking, Manegold and Hofmann (204) assumed the sieving to be expressible by the equation

$$\frac{c_f}{c_s} = \varphi \tag{11}$$

where c_f is the concentration of a momentary small volume of filtrate, c_s is the simultaneous concentration of the filtering solution, and φ is the "sieve constant," independent of c_s. The value of c_s, and the concentration of the total filtrate at any point, are obtainable by integration of appropriate differential equations. The integrals were evaluated for various conditions (a closed system; a system in which the original solution is continuously added to keep the volume of filtering solution constant; a system in which pure solvent is added at intervals to keep up the volume of filtering solution; etc.). For filtration in a closed system, where nothing is added or removed, the concentrations of both residue and total filtrate should increase with time (the latter much more slowly), when the sieve constant is neither 0 nor 1. Such a concentration increase in both residue and filtrate has been reported by Cox and Hyde (76) for filtration of colloidal dyes through Bechhold membranes, and by Duclaux and Hirata (84) for filtration of gelatin through uncalibrated sacs.

2. Statistical evaluation of the sieve constant

The significance of the sieve constant in terms of sizes of pores and solute particles remains to be discussed. For a perfectly monodisperse solute and a perfectly isoporous filter, it has usually been implicitly assumed that the solute would either pass in undiminished concentration ($\varphi = 1$), or be entirely retained ($\varphi = 0$), depending on the relative sizes of pores and particles. This viewpoint must be, however, erroneous. The proportions of solute and solvent which pass the membrane depend on statistical considerations, even when the solute particles are so large that the water can be considered continuous by comparison. The sieve constant should increase gradually from 0 to 1 as the pore size is progressively increased above the end-point value.

On the basis of several simplifying assumptions, it is possible to calculate φ as a function of the ratio of pore size to particle size (119). It is assumed that:

(1) The membrane structure is represented by structure (a) of page 387 and is ideally isoporous.

(2) Adsorption and blocking are absent.

(3) Every solute particle is travelling vertically downwards when its center passes the plane of the surface of the membrane, and, in order to penetrate a pore, it must be wholly within the walls of the latter; i.e., its center must lie within a circle of radius $r - R$, where r is the radius of the pore[7] and R that of the particle.

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[7] The pore radius in this case is not that determined by the usual calibration methods, but is the effective radius in filtration, defined on a scale such that $r \leqq R$ for membranes completely impermeable to the solute. This question is more fully discussed in a paper in press in the Journal of General Physiology.

(4) At the mouth of the pore there is no radial component of the hydrodynamical velocity of flow, and the vertical velocity has a parabolic distribution across the capillary in accordance with Poiseuille flow.

(5) The solution above the membrane is homogeneous, thermal motion preventing any accumulation of particles at the mouth of the pore.

In this case, the expression for the sieve constant is evaluated as

$$\varphi = 2\left(1 - \frac{R}{r}\right)^2 - \left(1 - \frac{R}{r}\right)^4 \tag{12}$$

The sieve constant φ is plotted in figure 16 as a function of the logarithm of the ratio r/R. This theoretical curve closely resembles the experimental end-point curves for normal filtration shown in figure 7. Several significant values of r/R are noted for reference: (a) For $\varphi = 0.50$ (first indication of fall in filtrate concentration detectable in most viruses), $r/R = 2.18$. (b) For inflection point in curve, $r/R = 1.41$. (c) For end points (i.e., apparent complete retention of disperse phase): in chemical substances, $\varphi = 0.001$, $r/R = 1.022$; in bacteriophages and viruses, $\varphi = 10^{-6}$, $r/R = 1.0007$; theoretical end point, $\varphi = 0$, $r/R = 1.0000$.

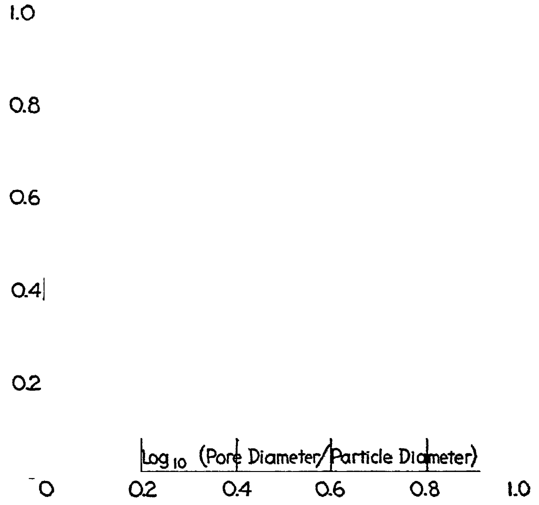

FIG. 16. Theoretical curve for the sieve constant as a function of the logarithm of the ratio of pore diameter to particle diameter

A sieving effect—i.e., the partial transmission of the solute, to an extent which varies with the membrane porosity—can thus be anticipated on purely statistical grounds. This indicates as invalid an assumption often implicitly accepted in the literature, that a sieving effect must be due either to polydispersion in the system filtered or to heteroporosity in the filters employed.

3. Statistical sieving in the absence of isoporosity and monodispersion

In practice ideal isoporosity is never attained, and probably colloidal solutions are never perfectly monodisperse, although some proteins approach this condition closely. When the statistical frequency of pores (or particles) of different sizes is given by a distribution function which is not a sharp peak, the curves of the type of figure 7 or figure 16 are less steep, and sieving occurs over a greater range of filter porosities than is the case for isoporosity and monodispersion, while the apparent end points for chemical and bacteriological systems are much farther apart.

4. Effect of stirring on sieving

The considerations of Manegold and Hofmann (204) hold only in a system where the residue is always homogeneous; i.e., when the rate of filtration is slow compared with diffusion, or when local concentration immediately above the filter is prevented by stirring or agitation. Ershler (115) has discussed the situation where diffusion is negligible, so that the whole of the retained solute remains locally concentrated in a layer of solution just above the surface of the membrane. The concentration of this layer increases until it attains a value c_s/φ, where c_s is the concentration of the body of the filtering solution; then it remains constant throughout the filtration. After the concentration of this layer above the membrane becomes constant, the filtrate has a constant concentration c_s, and the solute apparently passes through the filter unhindered. This effect was demonstrated experimentally for filtration of electrolytes through dense membranes (part IV, A, 3).

G. CONTRAST BETWEEN DIALYSIS AND ULTRAFILTRATION

It has been often pointed out that permeability in dialysis and permeability in ultrafiltration are not comparable. Levy (177) showed that certain collodion sacs were impermeable to ptyalin, rennin, and pepsin in ultrafiltration, but that these enzymes could dialyze through the sacs. Bechhold (16) noted that oxalic acid was separable from colloidal Prussian blue by dialysis, whereas ultrafiltration of the mixture only resulted in a precipitation on top of the membrane. Elford and Ferry (103) found that, although a membrane of porosity 45 mμ was impermeable to isoelectric serum albumin in ultrafiltration at 3 atmospheres pressure, the isoelectric protein could diffuse through a membrane of porosity 14 mμ. It is probable that in diffusion or dialysis, where the penetration of the disperse phase into the membrane takes place by molecular motion only, the effects of blocking are absent, so that dialysis end-point porosity should be about the same as that found in "normal" filtration.

IV. Experimental Results of Ultrafiltration of Disperse Systems

The previous section has shown the influence of experimental conditions upon the results of ultrafiltration. In applications to the fractionation and study of composition of disperse systems, it is difficult to compare data unless the experimental conditions are completely described,—which has been too rarely the case. Unfortunately, also, much of the earlier work has been done with filters which were characterized imperfectly or not at all. Even in this case, however, some significant comparative results have been obtained.

A. ULTRAFILTRATION OF COLLOIDS AND CRYSTALLOIDS

1. Composition of colloidal sols

Bechhold's original investigations (16, 17) included ultrafiltration of numerous colloidal systems. Heterodispersion of particles in a silver sol was demonstrated by filtration of two fractions which had been prepared by centrifugation; a filter was found which passed the particles of one fraction and retained those of the other. End points of sols investigated were arranged in descending order: Prussian blue, platinum (Bredig), ferric hydroxide, casein, arsenic trisulfide, gold (40 mμ), silver (20 mμ), gold (1 to 4 mμ), 1 per cent gelatin, 1 per cent hemoglobin, serum albumin, diphtheria toxin, protoalbumoses, silicic acid, lysalbumin, deuteroalbumoses A, B, and C, litmus, and dextrin.

Malfitano (199a) studied the composition of colloidal ferric hydroxide, stabilized with hydrochloric acid, by ultrafiltration. The ultrafiltrates (i.e., colloid-free filtrates) contained only hydrochloric acid, and repeated ultrafiltrations (adding water to make up the volume above the filter) resulted in continued hydrolysis, with eventual coagulation of the colloid, the coagulation being to some extent reversible by addition of more hydrochloric acid. Wintgen and Biltz (286b) employed ultrafiltration in conjunction with measurements of conductivity and transference to study the composition of ferric hydroxide micelles. McBain and McClatchie (195), using membranes of cellophane, showed that the composition of ultrafiltrates from a ferric hydroxide sol varied greatly with the rate of filtration; the concentration of simple electrolytes in the filtrate (measured by conductivity) fell off fourfold for a sixfold increase in rate. This is the result to be expected from a blocking effect, but the authors point out that the mutual repulsion of the colloidal particles would prevent blocking (the particles being assumably too large actually to enter the pores), and attribute the results to an internal Donnan effect. The concentration of the intermicellar fluid varies from point to point, being the least in the immediate neighborhood of the micelles. The ultrafiltrate at zero pressure, or dialyzate of the sol, gives the composition of the dispersing medium far from the influence of the micelles, and is the most concentrated ultrafiltrate obtainable. In filtrations at increasingly high pressures, the micellar domains (ionic atmospheres) are drained to an increasing extent, and the ultrafiltrates correspondingly diluted. Mukherjee et al. (221), on the other hand, reported ferric hydroxide ultrafiltrates of a higher conductivity than that of the original sol.

McBain and Jenkins (188), using Bechhold membranes, ultrafiltered soap solutions, whose colloidal and crystalloidal composition had been previously deduced from osmotic and conductivity measurements. The concentrations of ultrafiltrates through very dense membranes (maximum pore size less than 9 mμ) represented the concentrations of the crystalloidal components, which agreed with the previous data for solutions of sodium laurate below 0.8 N and sodium oleate below 0.5 N. The ultrafiltrate concentration was independent of pressure over a wide range. Very dilute, fresh solutions (0.01 N) of the soaps were completely ultrafilterable, showing absence of colloidal components. In sodium oleate, a fractionation was effected by membranes of maximum pore size from 15 mμ to 75 mμ, the sieving being independent of porosity over this range. This was attributed to separation of ionic micelles from neutral micelles, the former passing the filters and the latter being retained. The concentrations of ionic micelle and neutral colloid thus calculated from ultrafiltration were in agreement with conductivity and freezing-point data. The alkalinity of colloid-free ultrafiltrates was a measure of the degree of hydrolysis of soap solutions. McBain and Lucas (189) filtered 0.6 N sodium palmitate through No. 400 cellophane at 90°C.; the filtrate was 0.24 N in sodium palmitate, which agreed with the concentration of simple crystalloidal soap at this temperature and concentration deduced from conductivity and dew-point lowering.

Zsigmondy and Carius (295), using Zsigmondy–Bachmann membranes, studied ultrafiltration of sols of mercury, arsenic trisulfide, antimony trisulfide, and ferric hydroxide; all but the last appeared to be polydisperse, as evidenced by sieving. The possibility of statistical sieving was not, however, eliminated, in contrast to Bechhold's experiment with colloidal silver.

Wintgen (286a) used collodion membranes to prepare colloid-free ultrafiltrates of stannic acid sols. The proportion of alkali bound to the colloid was found to decrease with increasing alkalinity of the sol.

Wintgen and Löwenthal (286c) Ultrafiltered colloidal chromium hydroxide through Zsigmondy–Bachmann ultrafeinfilters. The greater the

Cl:Cr ratio in the micelles, the more readily filterable were the latter. In a given sol, the colloidal Cl:Cr ratio remained the same even when the suspension medium was ultrafiltered off and the residue re-suspended. Manegold and Hofmann (205) investigated the sieving of two chromium hydroxide sols through ether–alcohol collodion membranes. In the first sol, 25 per cent of the particles passed through membranes of average pore diameter[6] 6.6 mμ; 5 per cent more through 7 mμ; and 13 per cent more through 28 mμ. In the second sol, 30 per cent of the particles passed through a "Kongodicht" Ultrafeinfilter (porosity less than 6 mμ). By comparison of the experimental results with the theoretical filtration curve for a system where the residue is made up at intervals with the pure solvent, it was concluded that the sieve constant was, for some of the suspended particles, neither 0 nor 1.

Bechhold and Szidon (37), using impregnated membranes, ultrafiltered colloidal zinc sulfide, cadmium sulfide, ferric hydroxide, and collargol (silver), dispersed in benzene, toluene, petroleum ether, or linseed oil. The membranes (graded roughly in terms of the concentration of collodion in the impregnating solution) were calibrated by washing out the coagulating liquid (toluene) with alcohol and water and then determining the end points in filtration of hydrosols. The end points of the organosols (org.) and the calibrating hydrosols (aq.) are arranged in descending order: zinc sulfide (org.), cadmium sulfide (org.), Prussian blue (aq.), ferric hydroxide (org.), collargol (aq.), hemoglobin (aq.), collargol (org.), ferric and copper oleates (org.).

Most dyes in organic solvents (37) diffused through the densest Bechhold–Szidon membranes, and were concluded to be molecularly disperse (crystalloidal). This evidence was not, however, conclusive, since colloidal aggregates in reversible equilibrium with crystalloidal components may traverse a membrane by disaggregation, diffusion, and reaggregation. Ultrafiltration, on the other hand, rapidly separates colloidal components from crystalloidal before readjustment of equilibrium can be established. Ultrafiltration of dyes in aqueous solution was studied by Zsigmondy (293), using Zsigmondy–Bachmann membranes. All the dyes filtered more readily than gold sols, but less readily than sucrose. The end points of several are arranged in descending order: Benzopurpurin 4B, Wool black 6B, Congo red, Benzopurpurin 10B. By use of suitable membranes, it was possible to separate one dye from another. The marked difference in filterability between the two Benzopurpurins, whose molecular structures differ only in that the two methyl groups of 4B are replaced by methoxyl groups in 10B, was attributed to the greater hydrophilic character of 10B. Morton (218) studied the filtration of aqueous solutions of dyes at 75°C. through cellulose membranes of average pore diameter 2.1

mμ. Normal filtration obtained. The order of increasing filterability was Chlorazol fast orange AGS, Benzofast blue 8GL, Sky blue FF, Chrysophenine G. In each case, the filterability in the presence of sodium chloride improved markedly with increasing salt concentration up to 0.1 per cent, and for higher concentrations of salt gradually fell off. It was concluded that the degree of dispersion was the least in the absence of salt. An alternative explanation (243a) is that the effect of salt on the dispersion of the dye is always to decrease it, as evidenced by the filterability at higher concentrations, the impaired filterability in the complete absence of salt being due to electrokinetic effects which can be suppressed by small quantities of electrolytes.

Bhatia, Ghosh, and Dhar (44) studied the ultrafiltration of colloidal molybdic acid through membranes of ether–alcohol collodion impregnated in filter paper. These membranes retained colloidal ferric hydroxide. About 50 per cent of the molybdic acid in a sol freshly prepared from equivalent amounts of ammonium molybdate and hydrochloric acid was filterable. The fraction filterable decreased with time; it was decreased by addition of acid, increased by addition of base, and increased by dilution. All these effects suggest a partially reversible aggregation, such as would be expected for a lyophobic colloid, but do not demonstrate it conclusively, since the effects of blocking are not evaluated.

Kronsbein (167, 168) studied the ultrafiltration of colloidal silicic acid. He employed Zsigmondy–Bachmann filters, standardizing them by filtration of gold sols (with gum arabic as a protective colloid) whose particle sizes were estimated by ultramicroscopic count. The 40′ Ultrafeinfilters retained completely a gold sol of particle size 4 mμ, and were considered to effect a separation of colloidal from crystalloidal silicic acid. Under conditions where blocking was suppressed as much as possible (by dilution and stirring), the fraction of silica ultrafilterable from a fresh, well-dialyzed sol was 2 to 3 per cent; this decreased with time. A seventeen-year-old sol was 0.5 per cent filterable. Dilution did not increase the fraction filterable. Absence of colloidal silicic acid in the ultrafiltrates and of crystalloidal in the ultimate residue was demonstrated by a colorimetric method. Concentration of an ultrafiltrate by evaporation failed to reaggregate the crystalloidal silicic acid.

Hein and Späte (149), using uncalibrated collodion membranes, found that penta-*p*-bromotriphenylene-chromobromide dissolved in ethylene dibromide was retained in ultrafiltration experiments, and concluded that the solution was colloidal.

McBain and Kistler (193), using membranes of cellophane, ultrafiltered aqueous and non-aqueous solutions of several colloidal electrolytes. The membranes (maximum pore size 4 mμ to 6 mμ as shown by the bubble test) could pass benzene solutions of naphthalene and anthracene in undiminished concentration, but were considered to retain any colloidal constituents of a filtering system. Silver bromate dissolved in diethylamine was completely filterable at a concentration of 0.13 *N*, but at increasingly higher concentrations an increasing fraction of the salt was retained. A trace of water in the solution diminished the fraction retained. Silver nitrate dissolved in piperidine was retained to an extent which increased with the concentration. Similar retention was noted for ammonium iodide in aniline, barium perchlorate and cadmium iodide in amyl alcohol, cadmium iodide in ethyl alcohol, potassium acetate and pyridine in acetic acid, sodium acetate in 50 per cent acetic acid, and cadmium iodide, potassium iodate, and sodium iodate in water. This evidence for existence of colloidal constituents in these solutions supports the indications of anomalies in electrical conductivity and osmotic behavior.

Berczeller (41), using Bechhold membranes, ultrafiltered supersaturated aqueous solutions of menthol, thymol, and naphthol. The concentrations of the filtrates (measured by surface tension lowering) corresponded to saturated solutions, while the residues remained supersaturated; the supersaturated solutions were concluded to be partly colloidal.

2. Separation of colloids from crystalloids

The earliest collodion membranes (254, 246, 244) were of low porosity, and appeared to separate colloids from crystalloids effectively. The fact that collodion membranes do not always perform this separation perfectly was noted as early as 1903 by Gorsline (139), who used membranes which permitted diffusion of peptone, albumose, starch, dextrin, albumin, and certain enzymes. Application of suitable membranes, however, preferably under conditions of normal filtration, will permit the desired fractionation.

Bechhold (16) employed acetic collodion membranes for a practically quantitative separation of gelatin from glycine by ultrafiltration. Boëseken and Meyer (49), not succeeding in preparing collodion membranes sufficiently tight to retain dextrin, used membranes of copper ferrocyanide impregnated in collodion; these permitted reducing sugars to dialyze, but almost completely retained dextrin of molecular weight 5500. McBain (188, 190) has advocated cellophane for separation of colloids from crystalloids, employing it for study of various colloidal systems (see above). For more rapid separation of crystalloidal electrolytes from colloidal sols than can be effected by dialysis, electrodialysis, or ultrafiltration, electroultrafiltration may be employed (16, 150).

3. Sieving of crystalloids

Collander (75) studied the impeded diffusion of many organic acids and other compounds through flat collodion membranes, prepared in three porosity grades by the method of Brown. The rate of diffusion was related antibatically to the molecular size as measured by the molecular refractivities. Exceptions were phenol and *m*-nitrophenol, which diffused abnormally rapidly and were thought to be soluble in the membranes. To each membrane grade corresponded a maximum size of diffusible molecules.

Manegold (201) studied the diffusion of urea, sucrose, and hydrochloric acid through collodion membranes. For membranes whose pores were large enough to permit free diffusion, the results provided information concerning the membrane structure (part II, C, 2); for membranes through which the diffusion was impeded, the order of diffusibility was urea > sucrose > hydrochloric acid, in contrast to the order of free diffusion, hydrochloric acid > urea > sucrose. In general, in impeded diffusion, electrolytes encounter much more retardation than non-electrolytes.

Michaelis (216a) described dry collodion membranes which were permeable (in diffusion) to urea but not to glucose. These were permeable to univalent cations, but not to polyvalent cations nor any anions. This property gives rise to the Michaelis diffusion potential (page 394). Beutner, Caplan, and Loehr (43) suggest that the latter potential is due to chemical reaction between the salt and the collodion; this, however, seems unlikely, in view of its characteristic dependence on membrane porosity (part II, C, 2) and the fact that differential permeability to ions is shown by membranes of copper ferrocyanide as well as of collodion (75). This question is further discussed by Wilbrandt (285a).

Ershler (115), using rather thick ether–alcohol collodion membranes, reported that, under the same conditions of ultrafiltration, crystalloidal electrolytes might be retained to a much greater extent than non-electrolytes. The relative concentration of filtrate from a solution of a non-electrolyte was practically independent of the absolute concentration of the latter; for electrolytes, the relative concentration of filtrate increased markedly with increasing absolute concentration of the original solution. The degree of retention of an electrolyte was the greater, the higher the valence of the ion charged like the membrane, and the lower the valence of the ion charged unlike the membrane. This supported the explanation that the greater retention of electrolytes was due to repulsion of similarly charged ions from the pore walls, resulting in a diminution of the effective pore diameter.

McBain and Kistler (191) were able to separate methyl alcohol from sucrose in aqueous solution by ultrafiltration, using membranes of cellophane impregnated with collodion. Elford and Ferry (103) obtained collodion membranes, of average pore diameter about 2 mμ, which retained 95 per cent of a 1 per cent solution of sucrose in ultrafiltration.

As concerns permeability to crystalloids, three types of membranes can thus be distinguished, listing the order of decreasing porosity: (1) membranes of porosity greater than 4 to 5 mμ, such as the first cellophanes, through which all crystalloids filter in undiminished concentration; (2) membranes of the Ershler type or the McBain and Kistler impregnated type, which effect a certain sieving of non-electrolytes, and a much greater retention of electrolytes due to electrostatic repulsion of the anions of the latter; (3) membranes of the Michaelis type, which are impermeable to all but the smallest non-electrolyte molecules, and to all electrolytes by virtue of exclusion of their anions.

4. Determination of degree of hydration

The hydration of solute particles may be determined by ultrafiltration by using a reference substance which passes a filter retaining the solute in question. It must be assumed that the reference substance does not affect the solvation equilibrium and is itself not solved, and that the ultrafiltrate represents the interparticulate fluid far from the influence of solvation. Then the filtrate appears to have been concentrated in the reference substance because of retention of solvated solvent.

In this way, McBain and Jenkins (188), using potassium chloride as a reference substance, determined the hydration of potassium laurate to be approximately twelve water molecules per soap molecule. The extensive study of McBain, Kawakami, and Lucas (189) showed that this value was independent of the concentration of soap or salt at high ionic concentrations; internal Donnan effect was shown to be then suppressed. At low ionic concentrations the Donnan effect enters, and causes the apparent hydration to be two to three times as great.

McBain and Kistler (192), using methyl alcohol as the reference substance, obtained a figure for the hydration of sucrose of four molecules of water per molecule of sugar.

Greenberg and Greenberg (144) ultrafiltered solutions of gelatin, casein, starch, glycogen, and serum through uncalibrated sacs. Urea and glucose, as well as salts (in the isoelectric protein solutions), were used as reference substances for estimating the degree of hydration. The fraction of "bound" water was found in every case to be negligible within experimental error. It was concluded that the stability of these lyophilic colloids did not depend on a marked hydration, but more likely on molecular orientation on the particle surfaces.

B. ULTRAFILTRATION OF COLLOIDS OF INDUSTRIAL INTEREST

1. Petroleum

Bechhold and Szidon (37) ultrafiltered Trinidad asphalt in benzene solution through their impregnated membranes. Repeated washing with benzene effected passage of 32 per cent through a membrane which represented the end point for aqueous hemoglobin. The residue would not redissolve. • The retention was shown to be caused by specific adsorption by the collodion. Attempts to ultrafilter petroleum were unsuccessful.

Zaharia and Lucatu (289) ultrafiltered petroleum through membranes of vulcanized rubber at a pressure of 150 atmospheres. All paraffin, and the resins separable by 70 per cent ethyl alcohol, passed the filter; hard and soft asphalts were retained. The asphalt residue redissolved readily in the ultrafiltrate, or in benzene or cyclohexane, but, when solutions in any of these solvents were refiltered, the asphalt was again retained. It was accordingly concluded to be present as a lyophilic colloid.

2. Nitrocellulose and viscose

Kumichel (173), using Cella filters and the apparatus of Brukner and Overbeck, studied the ultrafiltration of nitrocellulose. The water in the filter pores was first replaced by the nitrocellulose solvent,—ordinarily acetone. By using a filter of sufficiently low porosity, an ultrafiltrate of practically pure acetone was obtained. Fink, Stahn, and Matthes (122) ultrafiltered viscose through special membranes prepared from an alkylated cellulose thiourethan dissolved in a volatile solvent such as pyridine, with addition of small quantities of a non-volatile solvent such as glycerol chlorohydrin to adjust the porosity. Ultrafiltrates of viscose solutions through such membranes were practically cellulose-free. The degree of esterification of the cellulose xanthate, as determined by ultrafiltration, was in satisfactory agreement with that determined by chemical means. The ultrafiltration data also permitted calculation of the amount of alkali adsorbed by the viscose.

3. Other systems

Miscellaneous applications of ultrafiltration to industry include the filtration and concentration of latex by Bechhold–König filters (79); separation of tannins from non-tannins (271, 58); ultrafiltration of fats and oils to reduce the tendency for them to become rancid (287); purification of switch and transformer oils (268); purification of water, removing a large proportion of the ash and silica (155); purification of gelatin and glue (28); ultrafiltration of opium to yield a principle free from fats, resins, wax, and proteins (212); purification of the active principles of belladonna, henbane, and strophanthus (51a); estimation of dextrin in beer (258); analysis of the salt content of soils by removing the electrolytes by electro-ultrafiltration (274, 165); and recovery of cholesterol and higher fatty acids from wool wash-waters (2).

C. ULTRAFILTRATION OF PROTEINS

1. *General properties of proteins*

Proteins are of particular interest in ultrafiltration, because of the monodisperse character of their solutions and their physical and chemical resemblance to many biological materials of greater complexity. The results of ultrafiltration of proteins may be interpreted in the light of the following characteristic properties.

a. Molecular weights. Svedberg (265) has shown by ultracentrifugation that solutions of most proteins are remarkably monodisperse, and that in most cases the particles do not depart markedly from spherical form. Gelatin and casein are the most common exceptions in being polydisperse. The molecular weights are in many cases approximate integral multiples of 34,000. Certain respiratory proteins have huge molecular weights, that of hemocyanin from *Helix* being 5,000,000. The molecular weight is independent of the pH over a limited range (the Svedberg stability range), usually from pH 4 to 9, except for a slight tendency to reversible aggregation at the isoelectric point. Outside of the stability range, breakdown of the molecules occurs, to varying degrees.

b. Amphoteric properties. A protein particle is usually considered as zwitterionic at the isoelectric point. On the acid or basic side, the protein acquires a net positive or negative charge respectively, due to collection of of hydrogen or hydroxyl ions respectively,—a process which may be considered equally well as chemical combination or Langmuir adsorption (154a).

c. Denaturation. Treatment of proteins by heat, strong acids and alkalis, alcohol, urea, and other reagents causes a reduction of the solubility in water, termed denaturation. Heat denaturation does not affect the molecular weight or cataphoretic mobility, but (in the case of egg albumin) alters the optical activity, refractivity, viscosity, absorption spectrum, and immunological properties of solutions (9). Complete denaturation is characterized by total insolubility at the isoelectric point. Egg albumin—but not serum proteins—is denatured when adsorbed in a surface film (210).

d. Adsorption of proteins. Most of the data on adsorption of proteins refer to saturation values, corresponding to the flat portion of the Langmuir adsorption isotherm. Hitchcock (154), studying the adsorption of gelatin on collodion membranes as a function of pH, found a marked maximum in adsorption at the isoelectric point; on the alkaline side, it fell off; on the acid side, it fell off sharply to a minimum and then increased with increasing acidity. A similar peak at the isoelectric point was found by Palmer (231), who showed further that addition of sodium chloride to non-isoelectric solutions increased the adsorption to the high isoelectric value. Maxima in adsorption by collodion were found by Ettisch et al. (116) for serum albumin at pH 4.7, serum globulin at 5.3, egg albumin at 4.7, and hemoglobin at 6.7.

Elford (94, 96) studied the adsorption of egg albumin, serum albumin, and serum pseudo-globulin on collodion, quartz, kieselguhr, and kaolin; each protein showed a sharp peak at the isoelectric point (figure 17), the shape of the curve being independent of the nature of the underlying surface. This independence of the underlying surface is also revealed by the cataphoresis experiments of Dummett and Bowden (85) for gelatin adsorbed on particles of quartz, carbon, and copper. This suggests that the peak adsorption at the isoelectric point involves adsorption of protein on protein, i.e., formation of multiple adsorbed layers. In contrast to the egg albumin and the serum proteins, hemoglobin does not have a great tendency to form multiple adsorbed layers, as shown by the specific effect of the underlying surface on cataphoretic mobility of hemoglobin-coated particles (85) and the smaller absolute amount of adsorption (saturated) at the isoelectric point (96). Of the serum proteins, the peak for globulin is much less sharp than for albumin, suggesting a tendency for multiple layer adsorption which extends over a broader pH range. The tendency for excessive adsorption may be identified with colloidal instability, tendency to aggregation, and perhaps with denaturation; and clearly with blocking and abnormal filtration (see below).

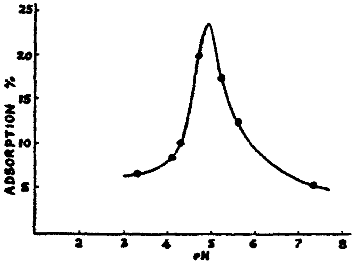

FIG. 17. Adsorption of horse serum albumin by collodion particles, plotted against the pH (94)

2. Filtration of single proteins

Risse (242) showed the effect of pH on the filterability of serum albumin and globulin and hemoglobin, each protein being least filterable at approximately its isoelectric point. Elford and Ferry studied in detail the ultrafiltration of 0.5 per cent solutions of horse serum albumin and pseudo-globulin (100) and egg albumin, edestin, and hemocyanin (101) through graded collodion membranes, determining the influence of various physical factors, as described below.

a. Influence of solvent medium. In comparative experiments in different solvents at comparable pH values (about 7.2 in each case), filtering through membranes of equal porosity (the value depending on the nature of the protein), the effect of each solvent medium is shown by the form of the filtration curve and the maximum relative concentration of filtrate attained. For egg albumin, serum albumin, serum pseudo-globulin, and hemocyanin, media arranged in the order of increasing favor to filtration are: water (0.05 per cent sodium chloride for globulin); 1.0 per cent sodium chloride, extra-digested Hartley's broth; standard Hartley's broth; Hartley's ox-heart broth. For the albumins, at pH about 7.2, all the solvents permit "normal" filtration; for the pseudo-globulin, normal filtration occurs only with standard or ox-heart broth; and, for the hemocyanin, only broth permits a filtration curve approaching the normal form. In the case of egg albumin and hemocyanin, $M/15$ phosphate buffer favors filtration slightly more than does 1.0 per cent sodium chloride. For edestin, Hartley's broth is much more favorable than 1.5 M sodium chloride.

b. Influence of pH. For egg albumin, serum albumin, and serum pseudo-globulin, the filterabilities have been studied over wide ranges of pH. The variation of the end-point porosities of the three proteins with pH is shown in figure 18. The solvent is water for the albumins, and 1.0 per cent saline for the globulin. For the globulin, the corresponding filtration curves are all abnormal. For the albumins, they are abnormal from pH 4.2 to 7, and normal on the acid or alkaline side of this zone (the boundaries not being sharply defined). The pH zone of abnormal filtration—i.e., blocking—corresponds exactly to the zones in which the end points are excessively high (figure 18), and also to the zone in which excessive adsorption of protein on collodion occurs (figure 17). This suggests that, for proteins, at least, blocking is due to multiple layer adsorption or colloidal instability (100). The dissymmetry in the end-point peaks may be attributed to the charge on the collodion, which is negative throughout, so that on the alkaline side there is a certain repulsion between membrane and protein.

In Hartley's broth as a solvent, the pH zone of abnormal filtration for the albumins is diminished to the narrow range of pH 4.3 to 5.5. For serum pseudo-globulin, it is diminished from extension beyond Svedberg's stability range (outside which the protein is no longer monodisperse) to a limit of about pH 7 on the alkaline side.

It is to be noted that the influence of pH on filterability of proteins does not necessarily imply formation of secondary aggregates in the neighborhood of the isoelectric point. Such aggregates are, in fact, not revealed in the work of Svedberg; although the latter relates to solutions of lower concentration. That there might be structural aggregates of a type which would not be revealed in ultracentrifugation, however, is suggested by certain properties of jellies (187).

The influence of pH on the filterability of proteins is of importance in the filtration of enzymes, toxins, and viruses, which behave in many ways like proteins, and filter generally more readily in alkaline than in acid solution (243, 5, 219, 228, 229, 97). The acidification of such systems is not carried very far (owing to the destruction, in most cases, of biological activity in acid solution), probably not beyond the isoelectric zone (pH 4.5 to 6); this accounts for the lack of observations of ready filterability on the extreme acid side of the pH range, such as noted for proteins.

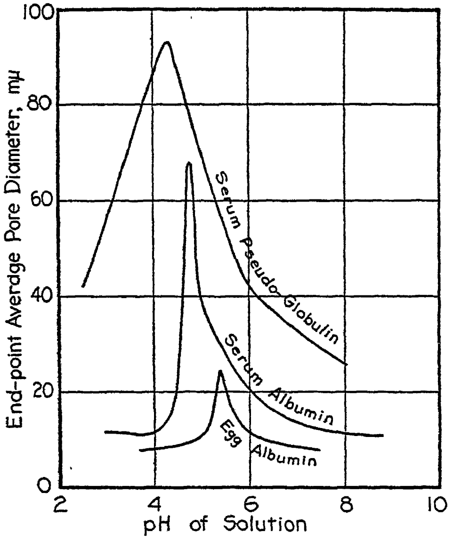

FIG. 18. Dependence of filtration end-point porosity on pH, for proteins (100, 101)

c. Influence of temperature. Duclaux and Hirata (84) found that the filterability of gelatin increased with temperature from 25° to 70°C.

d. End points. The end-point curves (figure 7) for filtration of proteins are steep, their form being quite similar to that predicted for sieving of a monodisperse system (figure 16), in agreement with the monodisperse character of proteins shown by Svedberg. The end-point porosities for different proteins under conditions where normal filtration obtains, but within Svedberg's pH-stability zone, are listed in table 2. The values are taken from Elford and Ferry (100, 101); in the case of the serum proteins, they are confirmed by Grabar (141)).

3. Filtration of artificial mixtures of the serum proteins

Elford and Ferry (100) noted that, at pH 3.8, membranes of average pore diameter between 40 mμ and 80 mμ completely retain serum pseudo-globulin (in 1 per cent sodium chloride) but pass albumin (in water) in undiminished concentration, when these proteins are filtered singly. In an artificial mixture of the two proteins in 1 per cent sodium chloride at this pH, the filterability of the globulin was increased and that of the albumin greatly decreased, both proteins partially passing a 70 mμ membrane and being retained by one of 40 mμ. This is probably not to be interpreted as due to an albumin–globulin complex (since some fractional sieving of the two proteins can actually be achieved in diluted serum, where the filtration is normal), but rather to the abnormal nature of the filtration of the globulin, which blocks up the pores to itself and to the albumin alike.

TABLE 2

Filtration end points of proteins

PROTEIN	SOLVENT MEDIUM	pH	END-POINT POROSITY
Egg albumin	Water	7.5	7–8 mμ
Egg albumin	Hartley's broth	7.6	6 mμ
Serum albumin	Water	8.0	11 mμ
Serum albumin	Hartley's broth	7.8	9-10 mμ
Serum pseudo-globulin	Hartley's broth	7.8	11-12 mμ
Edestin	Hartley's broth	7.6	18 mμ
Hemocyanin (*Helix*)	Hartley's broth	7.3	55 mμ

4. Composition of protein-free ultrafiltrates

Greenberg and Greenberg (143) prepared protein-free ultrafiltrates of alkaline solutions of casein by filtration through uncalibrated collodion sacs. The concentrations of added salts (sodium chloride, potassium chloride, sodium sulfate, potassium acetate) were always greater in the ultrafiltrate than in the original solution. The relative excess of salt in the filtrate (10 per cent to 80 per cent) was independent of the casein concentration, but decreased with increase in the absolute concentration of the salt. The concentration of urea in an ultrafiltrate was the same as in the corresponding original solution. These results indicate the influence of a Donnan effect.

Polanyi (235a) pointed out that the concentration of salt in the protein-free diffusate or ultrafiltrate of a protein solution does not exactly represent the concentration of free or unbound salt in the original solution, owing to retention of water of hydration by the protein, causing the proportion of unbound or diffusible crystalloid to appear too large. Augsberger (6) applied this principle to the recalculation of data on ultrafiltrates of serum (table 3). Eversole, Ford, and Thomas (117) compared the proportion of "bound" calcium in mixtures of gelatin and calcium acetate as determined by dialysis and by calcium electrodes. The former method, taking into account the Donnan distribution, gave considerably smaller figures for the bound calcium in the protein solution, as predicted on the basis of retention of water of hydration. The magnitude of hydration required, however, was far greater than that indicated by ultrafiltration (page 423).

D. ULTRAFILTRATION OF SERA

1. *Filtrations in which all protein is completely retained*

Ultrafiltration has been applied by many workers to the study of the composition of protein-free ultrafiltrates of body fluids, particularly blood serum. The work here quoted refers to mammalian sera, chiefly of the horse, ox, and man. The degree to which the various electrolytes present in serum and plasma are retained with the proteins has received the most attention. Results are usually expressed in terms of the percentage filterable, i.e., the relative concentration of the particular constituent in the filtrate as referred to the original serum.

a. Normal blood serum. The data of eleven papers on ultrafiltrates of normal blood serum and plasma are summarized in table 3.

With few exceptions, the results are in good agreement, considering the wide variations in techniques and procedures. The data for the difference in the filterabilities of calcium in serum and in plasma are, however, contradictory. In two cases, evidence was cited that the non-filterable portions of different constituents were actually bound to the protein and not retained in any other way. Thus, the nitrogen content of serum ultrafiltrates (286, 108) checked with the non-protein nitrogen of the original serum, i.e., the nitrogen content after the proteins were precipitated by trichloroacetic acid or the method of Folin and Wu. Also, the non-filterable fractions of sodium and potassium are equal to the fractions carried down with the proteins when the latter are precipitated by alcohol (178). However, the apparent binding of calcium to the serum proteins is about twice as great when they are precipitated by alcohol as when they are ultrafiltered off.

von Deseö and Lamoth (78) and Eissner (88) studied the variation in serum ultrafiltrate concentration with the volume filtered. In the former investigation, Zsigmondy–Bachmann Ultrafeinfilters were employed, and physiological saline, followed by Ringer's solution, was first passed through these to saturate them with the salts present in serum. Both reports showed a slow increase in the total concentration of solutes in the ultrafiltrate as the filtration proceeded. The ratio of sodium to chloride remained unaltered (88). The effect was attributed to progressive increase in the retention of water of hydration in the residue, as the concentration of protein increased there. In view of the fact that the rate of filtration decreased with time (78), an alternative explanation may be an inner Donnan effect, which corresponds to the suggestion of Ambard and Deviller (1a). Wilenskii (286) found that the nitrogen content of the ultrafiltrate was independent of the volume filtered, giving a flat filtration curve.

TABLE 3

Composition of protein-free ultrafiltrates of serum and plasma (expressed in relative concentrations referred to the filtering solution)

AUTHOR	TYPE OF MEMBRANES	PERCENTAGES FILTERABLE								
		Cl	Na	K	Ca	Mg	P	N	Urea	Sugar
		Serum								
Rona and Takahashi* (245a)					63–75					
Cushny (77)	Walpole sacs	100	100	100	62–70				100	
Tschimber and Tschimber (275)	Giemsa sacs		100		50–60	70	30			
Richter-Quittner (241)	Giemsa sacs			0						100
Blum and Delaville (48)			100	100	Part	Part	Part			
Augsberger (6)†			90		57–69	70–80				<100
Wilenskii (286)‡	Special sacs									
Lévy and Pacu (179)		100	90	95	64	60–70				
Schmidt-Hebbel (249)					70–73					
Bendien and Snapper (40)	Special sacs				50					
Watchorn and McCance (283)					57	75				
		Plasma								
Wilenskii (286)‡	Special sacs							3		
Lévy and Pacu (179)		100	90	95	72	60–70				
Schmidt-Hebbel (249)					50–55					

* Diffusion, not ultrafiltration.
† Recalculations of various data.
‡ Serum or plasma diluted 1:10.

Eissner (88) reported that when the pH of serum (normally about 8.0) is altered to 5.8, the calcium becomes almost completely filterable. The influence of added salts on the filterability of calcium at constant pH was studied with acetic collodion membranes by Brull et al. (64), who found that different ions increased the filterability in the order of a Hofmeister series: citrate > tartrate > chloride > iodide > thiocyanate. The calcium became completely filterable at a salt concentration of about 0.05 *N*, except in the case of citrate, where 0.02 *N* was sufficient. The citrate ion was supposed to act directly on the calcium, rather than on the proteins.

The effect of pH and neutral salts on the velocity of ultrafiltration of diluted serum was studied by Ellinger and Neuschloss (112). Progressive increase in pH from 7.7 to 8.9 caused first an increase, then a decrease in the velocity. Salts decreased the velocity in the order of a Hofmeister series: citrate > sulfate > acetate > chloride > bromide > iodide > thiocyanate. Caffein in small amounts decreased the velocity at pH 8.4, but increased it at pH 7.1.

Brühl (59) determined organic acids in ultrafiltrates of normal and pathological sera. The normal concentration lay between 7.7 and 10.2 millimolar; in uremia, after tetanic cramps, and under a ketogenic diet, the concentration of acid was increased to a varying extent up to 29.5 millimolar.

b. Pathological blood sera. Blum and Delaville (48) noted that for certain pathological sera the relative concentration of sodium in ultrafiltrates is less, and that of calcium more, than for normal serum. Scholtz (251) stated that, in cases of shrunken kidney, the filterability of calcium was decreased. Watchorn and McCance (283) studied the filterabilities of calcium and magnesium in various pathological cases, and found, in general, little correlation of the results with diagnosis. In pregnancy, however, the non-filterable fractions were decreased.

c. Milk. Rona and Michaelis (245) found 40 to 50 per cent of the calcium in milk to be diffusible. Wha (285) studied both dialysis and ultrafiltration of milk. Most of the calcium was able to pass through collodion membranes in dialysis. In ultrafiltration, the relative concentration of calcium in ultrafiltrates of fresh milk was 50 per cent; of sour milk, 100 per cent. Potassium and chlorides passed the filter in undiminished concentration for both fresh and sour milk; phosphorus was 40 per cent filterable.

2. Filtrations in which sieving of proteins occurs

a. Filtration end points of proteins. Bendien and Snapper (40) ultrafiltered normal blood serum through collodion sacs of graded porosity. The albumin–globulin ratio was always higher in the ultrafiltrate than in the original serum, indicating that the albumin particles are smaller than the globulin and not bound to the latter in any complex. These observations are confirmed by the quantitative work of Elford, Grabar, and

Fischer (108). The end-point porosities of Elford membranes for the proteins in native serum are given in table 4 (100). These values are in agreement with the end points of the purified proteins dissolved in corresponding media (table 2).

The fact that the end point of albumin is lower than that of globulin, and that membranes of porosity somewhat greater than the end points of both proteins are more permeable to the albumin, accounts for the increased albumin–globulin ratio in the transudate of edema and in the urine of albuminuria.

b. Association of other constituents with protein fractions. Bendien and Snapper (40), by comparing the relative concentration of a non-protein constituent in a serum filtrate with the relative concentrations of albumin, of globulin, and of total protein in the same filtrate, were able to conclude to which protein fraction that constituent was bound. In this way, they found that the non-ultrafilterable or protein-bound calcium is probably bound by albumin alone. Bilirubin is also bound by albumin; lipochrome, not by the albumin nor by all the globulin; cholesterin and lecithin, not by the albumin nor by all the globulin, but perhaps partly bound by the euglobulin.

TABLE 4

End points of proteins in native serum

SERUM	pH	END POINT OF ALBUMIN	END POINT OF GLOBULIN
Undiluted serum	8.2	9–10 mμ	11 mμ
Serum:broth, 1:9	7.6-7.8	9–10 mμ	11 mμ
Serum:saline, 1:9	7.8-8.0	11 mμ	13 mμ

In a similar way, deKruif and Eggerth (172) used ultrafiltration through uncalibrated sacs to show that anaphylatoxins were associated with the globulin fraction.

3. Ultrafiltration in vivo

It is possible to lead the blood stream of an animal through an ultrafilter, after injection of heparin to prevent clotting, and thus to obtain an ultrafiltrate of the blood *in vivo*. A convenient apparatus is described by Geiger (132). Brull (63) performed this experiment, finding that chlorides, dextrose, and non-protein nitrogen passed the filter in undiminished concentration, while phosphorus and calcium were partially retained, i.e., the results were similar to those of ultrafiltration *in vitro* (table 3).

E. ULTRAFILTRATION OF CHEMICAL SUBSTANCES OF BIOLOGICAL ACTIVITY

1. Enzymes

Strada (264) filtered various enzymes (cleared by preliminary passage through filter candles) through uncalibrated collodion sacs. The pepsin of gastric juice was retained, but the hydrochloric acid was passed in undiminished concentration, showing that it was not associated with the enzyme. The trypsinogen of pancreatic juice and kinase passed the filter separately, but, when mixed, their proteolytic activity was retained. Bechhold and Keiner (26) found that enterokinase was retained by a 4 per cent Bechhold membrane, while trypsin passed a 10 per cent membrane. In weak alkaline solution, however, the kinase passed membranes which retained all protein. Lagrange and Suarez (175) filtered several enzymes through Bechhold–König filters; the order of increasing filterability was trypsin, lipase, vitellase, amylase. Jacoby (159) filtered urease through Zsigmondy–Bachmann membranes; the wide range of porosities over which apparent sieving occurred seemed to indicate that the enzyme was polydisperse. Grabar and Riegert (142a) employed Elford membranes in the ultrafiltration of urease; the activity was found to be associated with polydisperse particles of a protein nature. The end point of the most nearly homogeneous preparation was similar to that of serum globulin. In ultrafiltration of urease partially digested by tryptase, it was shown (142b) that the filterable breakdown products possessed none of the activity of the urease. Grabar (141a) filtered invertase through Elford membranes; the enzyme passed a membrane of porosity 13 mμ with little loss in concentration, while the end point was placed at 10 mμ. The particles were concluded to be similar in size to those of serum albumin (end point 9 to 10 mμ). Snell (260) employed membranes impermeable to amylase but permeable to more highly disperse substances for concentration and purification of malt extract.

2. Toxins and antitoxins

Bechhold–König filters have been used by Sierakowski and collaborators (180, 237) to concentrate and purify scarlatinous and diphtheria toxins. The latter has been purified by Wadsworth and Quigley (278) by concentration over impregnated ether–alcohol collodion membranes which retain all protein but pass 94 per cent of the nitrogen content of the unfiltered system. The residue, when diluted to the original volume, has undiminished activity, showing negligible adsorption. Zajdel (290) found that a 4 per cent Bechhold–König filter retained proteins, but passed diphtheria antitoxin; when the active, protein-free ultrafiltrate was filtered through a 10 per cent filter, the antitoxin was retained and concentrated, while salts and amino acids passed. Le Guyon (147) found that diphtheria toxin and antitoxin filtered about equally well, both passing at high concentrations collodion sacs which were impermeable to hemoglobin.

Bechhold (16) found it impossible to obtain ultrafiltration data for arachnolysin (poison from *Epeira diadema* spider) or stapholysin, due to strong adsorption by the acetic collodion membrane.

3. Other substances

Le Guyon (147), using collodion sacs which passed Congo red in undiminished concentration, found that pyocyanin (extracted from *B. Pyocyaneus* with chloroform) was completely ultrafilterable; so was tuberculin. Gough (140), in an extensive study of tuberculin, isolated two fractions, consisting of proteins and proteose, respectively. In filtration through Elford membranes, the protein fraction was retained at a porosity of 9 mμ; the proteose passed a membrane of porosity 4 mμ. W. Smith (259a), in a study of the "precipitating substance" from vaccinia virus, reported the end point of the former, determined by Elford, as 6 mμ; the particles of the precipitating substance were concluded to be similar in size to those of egg albumin. Krueger (169) prepared bacterial antigens by grinding bacteria and filtering through an acetic collodion membrane to remove debris. Burnet (66) separated a specific soluble substance from bacteriophage-lysed cultures of bacteria by ultrafiltering off the phage. Taylor, Braun, and Scott (267) found that insulin passed collodion membranes of various grades in undiminished concentration, once the primary adsorption was satisfied. Spain and Newell (261) ultrafiltered ragweed pollen extracts through cellophane. The hay fever allergen was present in the filtrate from No. 300 cellophane, but was retained by No. 1200. Grabar and Koutseff (142), in a study of ricin extracts, isolated two fractions, one toxic and the other allergic. In filtration through Elford membranes, the toxin was retained at a porosity of 7 mμ; the allergen passed membranes of porosity 4 mμ.

F. ULTRAFILTRATION OF BACTERIOLOGICAL SYSTEMS

Interpretation of ultrafiltration experiments with bacteriological systems, such as bacteriophages and viruses, on the basis of comparisons with chemical systems, such as colloids and crystalloids, frequently leads to erroneous conclusions. The marked differences between these two types of dispersions which must be taken into account in comparative studies are summarized in table 5.

The high dilution of bacteriological suspensions makes the effect of primary adsorption particularly marked; blocking probably enters only in the presence of gross foreign particles, which however are often present (tissue debris, etc.). The effect of heteroporosity is illustrated by comparison of a chemical and a bacteriological disperse system in filtration through a membrane whose *average* pore diameter is below the end-point porosity. The distribution of pore sizes may be spread to include a fair proportion of pores larger than the end point, and yet these large pores may not let through enough of the chemical system to be identified in the filtrate (i.e., 10^{13} particles per cubic centimeter). On the other hand, even a few large pores may let through enough bacteriological infective units for identification, since these can be detected in so much smaller amounts (24). For an ideally isoporous filter, however, on the basis of statistical sieving, the apparent end points of chemical and bacteriological systems are close together (within about 2 per cent); so, for comparing results of filtrations of the two types of systems, the filters employed should be as nearly isoporous as possible.

TABLE 5

Contrasts between chemical and bacteriological systems

	CHEMICAL SYSTEMS	BACTERIOLOGICAL SYSTEMS*
Concentration of filtering solution employed	10^{16} to 10^{19} particles per cc.	10^3 to 10^8 particles or infective units per cc.
Minimum concentration detectable	10^{13} to 10^{14} particles per cc.	1 to 10 particles or infective units per cc.
Minimum relative concentration detectable	$1/10^3$ to $1/10^5$	$1/10^3$ to $1/10^8$
Accuracy in determination of relative concentration	Two significant figures	Virus: a power of ten bacteria or phage: 1 significant figure
Effect of heteroporosity in filter	Spreading distribution of pore sizes may have little effect	Spreading distribution of pore sizes makes end point appear too small

* In the case of bacteria and bacteriophage, the infective unit is directly identifiable with the particle. For viruses, where analysis is possible only by animal inoculation, the infective unit is the minimal infective dose for the animal concerned.

Early work on the ultrafiltration of bacteriological systems is not reviewed completely here, attention being devoted principally to investigations in which the considerations of the preceding paragraph have been taken into account; and, in particular, the work of Elford, since it represents a series of studies carried out under uniform experimental conditions with a view to estimation of particle sizes. Estimations of the actual sizes of infective particles are discussed in part V.

1. Bacteriophages

A bacteriophage is a principle which, introduced into a culture of certain bacteria, multiplies within the cells, eventually killing and disintegrating or lysing them. d'Herelle, who discovered the phenomenon, showed that bacteriophage passed bacteria-tight filter candles, and that the concentration of a suspension of it could be estimated by plating successive dilutions on agar plates sown with the susceptible bacteria, the clear, sterile plaques appearing after incubation being ascribed to individual phage particles (cf. reference 24).

Early reports on ultrafiltration of bacteriophages represent an example of the untrustworthy conclusions arising from failure to consider the significance of table 5. Thus, it was deduced that the particles of phage were smaller than various proteins, or than strychnine nitrate molecules (cf. reference 98). This would have placed the particle diameter at less than 6 mμ. The more reliable work of Bechhold, Leitner, and Ornstein (27), taking into consideration the maximal pore sizes of the filters employed, placed the size of the smallest pores through which their phage could pass as about 40 mμ, while application of correction factors estimated the particle size as 55 mμ (24). The extensive investigation of Elford and Andrewes (98), employing highly isoporous membranes, showed that different strains of bacteriophage had different sizes, but all considerably larger than protein molecules—the end points ranging from 25 mμ to 110 mμ.

The end-point curve of Elford and Andrewes for each different phage strain was very steep, the first falling off in filtrate concentration being detected at a porosity about twice the end point. This resembles the result predicted for sieving of an ideally monodisperse system (part III, F), and indicates the high uniformity of particle size in each phage strain. The contrary statement, that bacteriophage is polydisperse, was made by Wollman and Suarez (288), reporting that Bechhold membranes of different porosities let through different concentrations of phage, but the range of porosities over which this sieving occurred was not great, and the effect may have been a simple statistical sieving. The experiments of Bronfenbrenner and Hetler (55), indicating that bacteriophage is not autonomous, but adsorbed on inactive particles, were not confirmed by Elford and Andrewes.

The filtration end point of a given phase was found to be independent of the organism on which it was cultivated. Different phages were adsorbed to about the same extent by collodion particles, showing that the differences in end points were not due to adsorption phenomena. Two phages of different end points could be separated by fractional ultrafiltration. By repeated washing of a phage suspension over a membrane which retained it, keeping up the volume of residue by addition of broth, it was possible to free the suspension from bacterial protein, with very little loss in the concentration of phage. Filtration of such a purified phage, when suspended in broth, gave the same results as that of the unwashed preparation, but in saline the purified phage filtered less readily, and the filtration curves were of the abnormal form, suggesting that purification had deprived the phage of a stabilizing agent. The actual end points of the different bacteriophage strains, following the serological classification of Burnet (65), are listed in table 9.

2. *Viruses*

The infective agents known as viruses have been commonly distinguished from bacteria by (1) their ability to pass bacteria-retaining filters, (2) their invisibility in the microscope, and (3) their failure to multiply in the absence of living cells (68). The early definition of these agents in terms of their ready filterability (as exemplified by the term "filterable virus"), dating from the first reports on tobacco mosaic in 1896 and foot and mouth disease in 1898, soon led to ultrafiltration experiments.

Suspensions of virus are difficult to obtain free from foreign matter which hinders filtration. In the case of plant-attacking viruses, the presence of sticky material from the plant tissues, which readily blocks ultrafilters, has long delayed the application of filtration methods. Viruses which attack animals are occasionally obtainable suspended in high concentration in body fluids, as foot and mouth disease in vesicular lymph from guinea pigs, and fowl plague in chicken serum. More frequently, however, the virus is found concentrated in some organ of the animal attacked, and often present in intracellular inclusions. The virus must be freed by grinding the tissues and breaking up the cells by autolysis and plasmoptysis. The resulting tissue debris and fatty materials must be removed before the suspension can be used for ultrafiltration experiments, on account of the blocking effects which arise from the presence of foreign particles. Centrifuging, filtration through coarse sand filters, and successive filtrations through collodion membranes of selected porosities well above the end point may serve to remove particles larger than those of the virus, leaving the latter in bacteria-free suspension, together with proteins and salts (10). Even the protein may be sometimes removed by washing the suspension over a membrane which retains the virus. Purification by adsorption and elution has been tried with varied success. Any drastic treatment is apt to inactivate the virus. The elimination of blocking effects by progressive purification of virus probably accounts for observations that the more highly a virus is purified, the smaller its particles seem to become. Too complete purification, however, may conceivably impair the filterability of a virus by depriving it of the capillary-active substances which aid filtration. It may also diminish the viability of the virus. Alteration of the pH, in particular, markedly affects the viability of most viruses, which rapidly become inactivated on the acid side of neutrality.

a. Foot and mouth disease. A very complete study of the ultrafiltration of foot and mouth disease was made by Galloway and Elford (129), using Elford membranes. The availability of small experimental animals of uniform susceptibility permitted a greater variety of experiments and more accurate analysis of filtrates than in most cases. There was no blocking, the filtration curves being normal in form. For filtrations through membranes of progressively lower porosity, the first marked diminution in filtrate concentration occurred at a porosity of 60 mμ, while the end point was 25 mμ. A mixture of the virus and coli bacteriophage (end point 65 mμ) could be quantitatively separated by a 65 mμ filter, while a 25 mμ filter quantitatively resolved a mixture of the virus and hemoglobin (end point 10 mμ). Variation of the pH between 6.4 and 8.7 for suspension in broth or phosphate saline was without effect on the filterability, in contrast to the marked superiority of alkaline reactions found by Busch (70) for the much more highly adsorbing Bechhold–König ultrafilters. The effect of medium, concentration, and membrane thickness on primary adsorption has been previously mentioned (part III).

b. Poliomyelitis. The particle size of the virus of poliomyelitis was estimated by Krueger and Schultz (171) from filtration through acetic collodion membranes as less than 300 mμ, and by Clifton, Schultz, and Gebhardt (73), who applied the same technique to a purified preparation, as less than 50 mμ. Elford, Galloway, and Perdrau (106) found the end-point porosity for filtration through graded collodion membranes to be 25 mμ, taking into account the low concentrations of the suspensions obtainable. Theiler and Bauer (269), using the technique of Elford, found an end point of 35 mμ; the filtration was, however, abnormal, with marked blocking, and the concentration of the virus suspension used was lower than that of Elford, Galloway, and Perdrau, so that a higher figure would be expected.

c. Louping ill. The virus of the louping ill of sheep was filtered by Elford and Galloway (105) through graded collodion membranes, the end-point porosity being determined as 40 mμ. It was possible to separate partially this virus from bacteriophage C36 (end point 60 mμ) and from bacteriophage S13 (end point 25 mμ) by suitable membranes.

d. St. Louis encephalitis. Bauer, Fite, and Webster (14a) ultrafiltered the virus of St. Louis epidemic encephalitis through Elford membranes, and found the end-point porosity to be below 66 mμ. Elford and Perdrau (109), using the same technique, placed the end point at a porosity of 60 mμ, in good agreement.

e. Yellow fever. Findlay and Broom (121) filtered yellow fever virus through Elford membranes, and found the end-point porosity to be 54 mμ. It was possible to concentrate the virus a thousandfold over membranes of porosity 50 mμ. Bauer and Hughes (15), employing the same technique, placed the end point at a porosity of 55 mμ, in excellent agreement.

f. Rift Valley fever. Broom and Findlay (56) applied the Elford technique to the ultrafiltration of Rift Valley fever virus, and placed the end point at a porosity of 70 mμ.

g. Fowl plague. Bechhold (22), using acetic collodion membranes, estimated the sizes of the largest pores which retained fowl plague virus to be 1.4 to 1.9 μ, and, by applying correction factors, judged the particle size to be 200 mμ. Elford and Todd (111), using Elford membranes, placed the end point at an average pore diameter of 125 mμ. When a mixture of the virus and Staph. K bacteriophage (end point 110 mμ) was filtered through a 125 mμ membrane, the virus was retained, and a trace of phage passed into the filtrate.

h. Vesicular stomatitis. Galloway and Elford (129a) filtered the virus of vesicular stomatitis, and placed its end point at a porosity of 0.13 μ, thus differentiating it markedly from foot and mouth disease virus. This result was confirmed by Bauer and Cox (14).

i. Borna Disease. Elford and Galloway (104) determined the end-point porosity in filtration of Borna Disease virus to be 0.175 μ. The end-point curve was not so steep as for most viruses, indicating possibly greater departure from uniformity in the particle sizes. The virus could be concentrated fivefold by filtering off the suspension medium through a 0.15 μ membrane. The virus could be easily separated from that of louping ill (end point 40 mμ) in a mixture of the two.

j. Newcastle Disease. Burnet and Ferry (69) ultrafiltered the virus of Newcastle Disease through Elford membranes, and placed the end point at a porosity of 0.16 μ.

k. Herpes. Zinsser and Tang (292) reported that herpes virus passed ultrafilters which retained colloidal arsenic trisulfide, but was retained by others which passed casein and fowl plague virus. Bedson (39a) filtered herpes through ether–alcohol and acetic collodion membranes, and found the end point to be sufficiently higher than those of the serum proteins to permit separation from the latter. That the end point of herpes is higher than that of fowl plague was confirmed by Elford, Perdrau, and Smith (110), who found the end point of the former to be 0.20 μ by the Elford technique.

l. Infectious ectromelia. Barnard and Elford (10) filtered the virus of infectious ectromelia through Elford membranes and placed the end point at 0.20 μ. It was possible to purify and concentrate the virus over a membrane of average pore diameter 0.11 μ.

m. Canary virus. Burnet (67) reported the end-point porosity of canary virus, as determined by Burnet and Elford, at 0.25 μ.

n. Vaccinia virus. Bechhold and Schlesinger (30) filtered vaccinia virus through Zsigmondy–Bachmann filters and deduced a particle size of 0.2 μ. Elford and Andrewes (97) studied the ultrafiltration through graded collodion membranes. The end point was placed at a porosity of 0.25 μ.

o. Rous sarcoma. Ultrafiltration of Rous sarcoma virus, and tumor extracts generally, is particularly difficult because of the presence of sticky foreign material which is very effective in blocking filters. Zinsser and Tang (292) found its behavior similar to that of herpes (see above). Mendelsohn, Clifton, and Lewis (213) quoted the end point for Bechhold membranes as 110 mμ. Elford and Andrewes (99) were able to rid the virus suspensions of unwanted constituents by washing above a membrane which retained the virus, and by filtration of such purified material placed the end point for Elford membranes at 0.15 μ to 0.20 μ.

3. Spirochetes

Hindle and Elford (152) found that, when suspensions of spirochetes were filtered at 37°C., the organisms passed filters of such low porosity as to assure that they were penetrating the pores "end-on," their length being at least 50 times their thickness. It was considered that coils and bends were perhaps straightened out while the spirochetes were traversing the pores. The filtrates were of low concentration, as would be expected from statistical considerations, since an organism must be suitably aligned with a pore in order to enter it, and this imposes a serious restriction. The end point of *Treponema pallidum* was judged to be 0.4 μ; of *Leptospira biflexa* and *Leptospira icterohaemorrhagiae*, 0.2 to 0.25 μ.

4. Bacteria

a. Filtrations in which sieving of bacteria occurs. Most early experiments on sieving of bacteria were made with filter candles of unglazed porcelain, which have a high adsorbing capacity. Mudd noted the influence of pH (cf. part IV, C, 2) and of motility (220); when the motility of *Vibrio percolans* was suppressed by anesthetics or cold, it was retained by filters normally permeable to it. Heymans (151) reported that the filterabilities of different bacteria parallelled the tendencies of their respective infections to spread in the organism. Elford (91, 94) studied the filterability of various bacteria through Bechhold and Elford membranes. The cells were somewhat deformable, so that the end point decreased with increasing filtration pressure. Values for the end points extrapolated to zero pressure, corresponding to absence of deformation of the bacteria, are given in table 6. The fact that the end points (in terms of average pore diameter) for the acetic collodion membranes lie below the true particle sizes indicates the heteroporosity of such membranes, considerable numbers of pores having diameters greater than the average value. The Elford membranes are evidently more nearly isoporous.

b. Filtrations in which all bacteria are retained. The advantages of large-pored collodion membranes over filter candles for preparation of sterile filtrates were pointed out by Eichhoff (87) and Meyeringh (215) for Zsigmondy–Bachmann membranes, and by Elford for his graded collodion membranes (93). Bacteria cannot grow through the membranes, which are, further, quite free from gross holes such as may occur in candles. The rate of filtration is substantially higher than through candles. The membranes may be used to obtain sterile suspensions of spirochetes (152), viruses, enzymes, proteins, and any thermally labile principles; while, even for thermally stable substances, they offer means of sterilization sometimes more convenient than heat. They also serve to concentrate highly dilute bacterial suspensions, so that the organisms can be identified visually (87).

TABLE 6

Filtration end points of bacteria

BACTERIUM	END POINT AT ZERO PRESSURE (AVERAGE PORE DIAMETER)		SIZE (MICROSCOPICALLY)
	Acetic collodion membrane	Elford membrane	
B. Coli	0.47μ		0.5–1μ by 1–2μ
B. Prodigiosus	0.43μ	0.75μ	0.75–1.0μ
B. Bronchisepticus	0.40μ		0.4μ by 1μ
Bovine pleuropneumonia (spheres)	0.35μ	0.35μ	0.2–0.25μ

V. QUANTITATIVE ESTIMATION OF PARTICLE SIZES

In the preceding section, remarks have been confined to the behavior of ultrafilters, characterized in various ways, in the filtration of different disperse systems; filtration end points have been quoted, expressed in terms of average pore diameter, without any attempt to deduce from these figures the sizes of the particles retained.

There are more direct methods than ultrafiltration for determining particle sizes. Of these, perhaps the most powerful at present is ultracentrifugation, applicable to both monodisperse and polydisperse systems. Accurate application of that method, however, as so far developed (265, 196) demands elaborate apparatus and a means of analyzing the system while in the process of centrifuging. The optical methods employed for analysis require a substantial concentration of the disperse phase and the absence of foreign constituents of similar optical properties. These conditions are in some cases difficult to fulfill. The technique of measurement of diffusion has not been developed to a point which permits quantitative estimation of particle sizes, although qualitative comparisons are possible. The most direct method of measuring the sizes of particles is by optical observation, which is applicable down to diameters of 0.2 μ, while, by application of ultra-violet photomicrography, particles of diameters as low as 0.10 μ may be resolved.

Ultrafiltration has been applied to estimation of particle sizes in cases where other methods are unsuited. The procedure consists in determining the filtration end-point porosity and applying to that figure an empirical correction factor representing the ratio, *diameter of particle/end-point average pore diameter.* The correction factor, which is itself a function of the end-point porosity, is determined by filtration of systems of known particle size.

A. EXPERIMENTAL REQUIREMENTS

In order that the correction factor (for a given end-point porosity) be the same for the system whose particle size is to be determined as for that whose particle size is known, experiments must be carried out under comparable conditions. In particular, normal filtration must obtain. For example, a comparison of the end points of serum albumin (figure 18), with the known particle size (5.4 mμ) shows that, in the center of the pH zone of abnormal filtration, the correction factor has the very low value of 0.12; while on either side, with normal filtration, it is as high as 0.5. Abnormal filtration is invariably associated with an abnormally low correction factor, and one which is more sensitive to slight modifications in experimental conditions, and unsuited for quantitative comparisons. The criterion of normal filtration, in terms of filtration curves (figure 6a, 6b), must be established. In selecting uniform experimental conditions, it is convenient to employ a capillary-active substance in the suspensions. For proteins and all protein-like systems, Hartley's broth at pH 7.4 to 7.6 has proved to be a suitable standard suspension medium. For lyophobic colloids, inorganic stabilizing agents are perhaps better.

The membranes used for quantitative comparative work must have high reproducibility and be highly isoporous. The most successful in this respect are those of Elford. The superiority of his technique is evidenced by the quantitative agreement in ultrafiltration results recently obtained by different laboratories employing it (part IV, F), in contrast to the complete lack of agreement in ultrafiltration studies which existed in the literature previously.

B. DETERMINATION OF THE CORRECTION FACTOR

Various authors have outlined tables of correction factors, notably Krueger and Ritter (170), Bechhold (23), and Elford (94), the values depending on the types of membrane used, the terms in which they were calibrated, and the experimental conditions adopted. However, owing to the superiority of Elford's membranes, and the greater volume of data to which his factors are applicable, his system is the only one here discussed.

TABLE 7

Determination of the empirical correction factor

PARTICLE	SIZE DETERMINED BY	PARTICLE SIZE, $2R$	END-POINT A.P.D. BY FILTRATION j_e	REFERENCE	RATIO $2R/j_e$
Bacillus prodigiosus	Microscopy (94)	0.5 –1.0μ	0.75μ	(94)	1.0 (average)
Bovine pleuropneumonia (spheres)	Microscopy (94)	0.25–0.3μ	0.35μ	(94)	0.8 (average)
Infectious ectromelia	Ultra-violet photomicrography (94)	0.13–0.14μ	0.20μ	(94)	0.67 (average)
Gold sols*	Ultramicroscopic count (94)	50–60 mμ	80 mμ	(94)	0.7
		35 mμ	60 mμ		0.6
		20 mμ	40 mμ		0.5
Hemocyanin (*Helix*)	Ultracentrifugation (265)	24 mμ	55 mμ	(101)	0.44
Edestin	Ultracentrifugation (265)	8 mμ	18 mμ	(101)	0.44
Serum pseudoglobulin	Ultracentrifugation (222)	6.9 mμ	11–12 mμ	(100)	0.6
Serum albumin	Ultracentrifugation (265)	5.4 mμ	9–10 mμ	(100)	0.57
Oxyhemoglobin	Ultracentrifugation (265)	5.4 mμ	10 mμ	(94)	0.54
Egg albumin	Ultracentrifugation (265)	4.3 mμ	6 mμ	(101)	0.72

* The capillary-active substance present in this case was not broth but sodium oleate.

The empirical correction factor for converting the end-point porosity (average pore diameter), for filtration in a standard solvent, to the particle diameter of the disperse phase was determined by Elford for various suspensions of known particle size, in Hartley's broth at pH 7.6 to 7.8. The results are summarized in table 7.

The empirical factor, $2R/j_e$, when plotted against the end-point porosity, is seen to pass through a minimum at about 25 mμ average pore diameter (figure 19, curve I). This is not surprising. It is to be expected that the ratio *particle size/true size of pores retaining particles* would decrease uniformly with decreasing pore size, as shown schematically in curve III. On the other hand, the ratio of the average pore size, as determined by the calibration methods of part II, D (page 398), to the true pore size, may be expected to fall off only slightly down to about 20 mμ, and then rapidly; this is shown schematically in curve II. The ratio of these two quantities thus estimated gives values for the ratio *particle size/end-point average pore diameter* which fall on the experimental curve, showing a minimum. The average pore diameter of calibration is always smaller than the true pore diameter, and the size of particles retained is always smaller still. Since the correction factor includes any discrepancy between the calibration porosity and the true dimensions of the pores, such discrepancy introduces no error in the estimation of particle sizes by application of the factor.

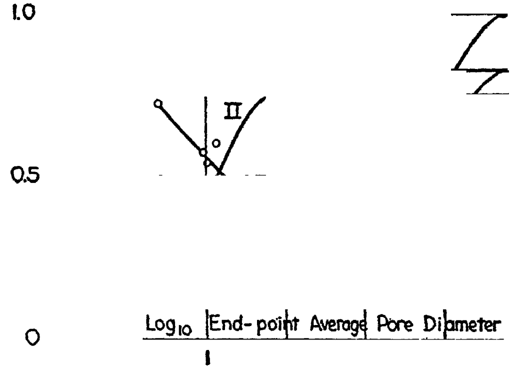

FIG. 19. Correction factors, plotted against end-point average pore diameter in mμ. Curve I, *particle size/end-point average pore diameter* (experimental). The circles refer to the determinations with proteins, viruses, and bacteria; the squares, to those with gold sols. Curve II, *average pore diameter as calibrated/true pore diameter* (schematic). Curve III, *particle size/true pore diameter at end point* (schematic).

Elford (94), in applying the correction factor, expressed it as a range between two values, as shown in table 8; this procedure has been followed by most other authors employing his technique.

C. APPLICATION TO BACTERIOLOGICAL SYSTEMS: EXPERIMENTAL RESULTS

Table 9 shows the particle sizes of various viruses, bacteriophages, and spirochetes, as quoted by Elford and other authors by application of the factors given in table 8. The last column gives the particle sizes as calculated from values of the factor obtained directly from figure 19; it is practically equivalent to the fourth column except for end points near 100 mμ, where Elford's factor changes abruptly.

The sizes of particles of bacteriological systems are thus estimated by correction factors which are determined, at the top of the porosity range, by filtration of other bacteriological systems, and, at the bottom of the range, by filtration of chemical systems. The error introduced by this last comparison (cf. table 5) is lessened by the isoporous qualities of the filters employed, but it certainly tends to make the figures quoted at the bottom of the list too small. Opposing this tendency are the effects of blocking by foreign bodies, which cannot always be eliminated, and the difficulty of saturating the primary adsorptive powers of even a thin membrane by dilute virus suspensions. These effects tend to make the estimated particle sizes too large, and it is on their account that Elford's factors (table 8) are displaced somewhat toward low values.

TABLE 8

Elford's use of the correction factor (94)

MEMBRANE AVERAGE PORE DIAMETER	FACTOR EMPLOYED
10 to 100 mμ	0.33 to 0.5
100 to 500 mμ	0.5 to 0.75
500 to 1000 mμ	0.75 to 1.0

The dependability of the particle sizes at the top of the list (where the factors, having been determined by filtration of bacteria, should be perfectly applicable) is borne out by ultra-violet photomicrography of virus particles (table 10). Another technique whose data can be compared with the filtration results is that of the bucket ultracentrifuge, a method developed by Bechhold and Schlesinger for ultracentrifugation of systems which must be sampled for analysis (29). This technique does not permit so thorough or accurate an analysis of a disperse system as that of Svedberg, but it has been successfully applied to different viruses and bacteriophages, and the results give remarkable confirmation of the relative sizes shown by filtration. The centrifuge places the absolute values higher (table 11). Again, diffusion experiments with different phages place them in the same order of increasing size as does filtration (98), although the significance of

TABLE 9

Estimation of particle sizes in bacteriological systems

PARTICLE	END POINT	ELFORD'S FACTOR (TABLE 8)	PARTICLE SIZE QUOTED BY AUTHORS	EXPERIMENTAL FACTOR (FIGURE 19)	PARTICLE SIZE FROM EXPERIMENTAL FACTOR
	mμ		*mμ*		*mμ*
Treponema pallidum spirochete* (152)	400	0.5–0.75	200		
Vaccinia virus (97)	250	0.5–0.75	125–175	0.7	175
Canary virus (67)	250	0.5–0.75	125–175	0.7	175
Leptospira spirochetes* (152)	200–250	0.5–0.75	100		
Herpes virus (110)	200	0.5–0.75	100–150	0.67	130
Infectious ectromelia virus (10)	200	0.5–0.75	100–150	0.67	130
Pseudo-rabies virus (105a)	200	0.5–0.75	100–150	0.67	130
Rous sarcoma No. 1 (99)	200	0.5–0.75	100		
Borna disease virus (104)	175	0.5–0.75	85–125	0.65	110
Newcastle disease virus (69)	160	0.5–0.75	80–120	0.63	100
Vesicular stomatitis virus (129a)	130	0.5–0.75	70–100	0.60	78
Fowl plague virus (111)	120	0.5–0.75	60–90	0.60	72
Bacteriophages Staph. K, D4, D12 (98)	110	0.5–0.75	50–75	0.59	65
Bacteriophages D54, S41 (98)	90	0.33–0.5	30–45	0.54	49
Rift Valley fever virus (56)	70	0.33–0.5	23–35	0.49	34
St. Louis encephalitis virus (14a)	66	0.33–0.5	22–33		
St. Louis encephalitis virus (109)	60	0.33–0.5	20–30	0.47	28
Bacteriophages C36, D13, D20, D48 (98)	60	0.33–0.5	20–30	0.47	28
Yellow fever virus (121)	54	0.33–0.5	18–27	0.45	24
Yellow fever virus (15)	55	0.33–0.5	18–27	0.45	25
Bacteriophage C13 (98)	45	0.33–0.5	15–20	0.43	19
Louping ill virus (105)	40	0.33–0.5	15–20	0.43	17
Bacteriophage S13 (98)	25	0.33–0.5	8–12	0.41	10
Foot and mouth disease (129)	25	0.33–0.5	8–12	0.41	10
Poliomyelitis virus (106)	25	0.33–0.5	8–12	0.41	10
Poliomyelitis virus (269)	35†	0.33–0.5	12–17		

* Diameter of spirochete quoted.

† Titer of virus lower than in experiments of reference 106.

TABLE 10

Sizes of virus particles: comparison between results of filtration and ultra-violet photomicrography (68)

VIRUS	SIZE OF INFECTIVE UNITS BY ULTRAFILTRATION	SIZE OF PARTICLES BY PHOTOMICROGRAPHY
Vaccina virus	0.125–0.175μ	0.15μ
Canary virus	0.125–0.175μ	0.16–0.17μ

calculation of absolute values of the sizes from diffusion is not established (24).

In the future, it is likely that these other physical methods will be developed to the point where they will yield more reliable determinations of particle sizes than ultrafiltration. Ultrafiltration will, however, when conducted under suitable experimental conditions, probably remain the most valuable technique for preparing homogeneous and homodisperse systems to which the more elaborate methods can be applied.

TABLE 11

Sizes of virus and bacteriophage particles: comparison between results of filtration and the bucket ultracentrifuge

PARTICLE	SIZE BY ULTRAFILTRATION		SIZE BY ULTRACENTRIFUGE
	Column 4, table 9	Column 6, table 9	
Bacteriophages: C16	50–75 mμ	65 mμ	90 mμ (247)
C21	30–45 mμ	49 mμ	75 mμ (247)
L	30–45 mμ	49 mμ	75 mμ (247)
D20	20–30 mμ	28 mμ	50 mμ (247)
S13	8–12 mμ	10 mμ	20 mμ (247)
Viruses: Vaccinia	125–175 mμ	175 mμ	200 mμ (30)
Canary	125–175 mμ	175 mμ	120 mμ (32)
Herpes	100–150 mμ	130 mμ	200 mμ (31)
Fowl plague	60–90 mμ	72 mμ	110 mμ (30)

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ARTIFICIAL RADIOACTIVITY

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I. HISTORICAL INTRODUCTION

On January 15, 1934, I. Curie and F. Joliot (26) observed for the first time the phenomenon which, under the name of "induced" or "artificial" radioactivity, had been sought since the discovery of the natural activity of uranium by Becquerel in 1896. In the course of their investigations of the positive electron, which had been discovered less than two years before, they found that when certain light elements (boron, magnesium, aluminum) were bombarded with the alpha-particles of polonium, they emitted positrons in large numbers. The discovery of artificial radioactivity was made when Curie and Joliot found that the emission of positrons from the bombarded elements did not cease immediately upon the removal of the source of alpha-particles, but instead decayed according to an exponential law, with a half-life of several minutes duration, characteristic of the substance bombarded.[2] They found that the growth of the activity under alpha-particle bombardment followed the usual exponential curve, the transformation constant being the same for growth and decay; after a time of irradiation, long as compared with the half-life of the substance under investigation, the activity produced in a sample reached a saturation value which could not be increased by further irradiation. The intensity of the artificial radioactivity was decreased by a reduction in the energy of the bombarding alpha-particles, but the half-life was independent of the energy with which the alpha-particles struck the target being activated. The new type of radioactivity is seen to be precisely the same in character as natural radioactive beta-disintegration, save for the two important differences that (a) the particles emitted are positive, not negative, electrons, and (b) the radioactive nuclei are derived, not from the preceding decay of a naturally radioactive parent, but from a nuclear transmutation phenomenon produced by the bombardment of a stable nucleus by a swift alpha-particle.

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[2] The half-life is the time required for the activity to decrease to one-half of its initial value.

It was subsequently found that magnesium emitted negative electrons as well as positrons after alpha-particle bombardment, and in such cases there is complete analogy with natural beta-decay, except for the mode of formation of the radioactive nucleus. In what is to follow, the radioactive emission either of positrons or of electrons will be indicated in each case. The energy distribution of the positrons ejected by an artificial radioactive element is, in all cases which have been examined, precisely similar in character to the continuous beta-particle spectrum which has long been known, and there is no reason for regarding radioactive positron emission as a phenomenon essentially different in nature from radioactive electron emission.

In their first paper, Curie and Joliot had ascribed the radioactivity induced in boron by alpha-particle bombardment to N^{13}, an isotope of nitrogen not known in nature, formed in accordance with the nuclear reaction[3]

$$_{5}B^{10} + {}_{2}He^{4} \rightarrow {}_{7}N^{13} + {}_{0}n^{1}$$

followed by

$$_{7}N^{13} \rightarrow {}_{6}C^{13} + {}_{1}e^{+}$$

They predicted that the same radioactive nitrogen could be formed by the bombardment of carbon with deutons, according to the reaction

$$_{6}C^{12} + {}_{1}H^{2} \rightarrow {}_{7}N^{13} + {}_{0}n^{1}$$

This prediction proved to be correct, and led to the first production of radioelements by totally artificial means, without the use of a naturally radioactive source of alpha-particles. Crane and Lauritsen (22, 24), Henderson, Livingston, and Lawrence (56), and later Cockcroft (17, 18) verified that an artificial radioelement was produced by the deuton bombardment of carbon. Cockcroft, Gilbert, and Walton (19) and Crane and Lauritsen (23) also demonstrated that the same N^{13} was formed by the proton bombardment of carbon, while Crane and Lauritsen had also found that boron displayed a radioactivity under deuton (22, 24) and proton (23) bombardment which they correctly attributed to C^{11}.

It was apparent that at the voltages available (up to about 3×10^6) for accelerating protons and deutons, and with the energies possessed (up to about 8.8 m.e.v. (million electron volts)) by alpha-particles obtainable from naturally radioactive sources, the nuclear transformations necessary to produce artificial radioelements could be brought about only in the lightest elements, viz., those having the lowest potential barriers opposed to the entry of charged particles into the nucleus. Fermi (43), therefore, tried the effect of neutron bombardment of various elements, in the hope of producing artificial radioactivity, as there is certainly no Coulomb field opposed to the entry of a neutron into a nucleus. From the first this method was successful, and Fermi and his coworkers have been able to produce transmutations leading to artificial radioelements in almost all of the elements.

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[3] The symbol $_{0}n^{1}$ is used to designate the neutron, a particle with no charge and a mass of 1.0085 ($O = 16.0000$). For the present purposes the symbols $_{Z}X^{A}$, $_{Z}W^{A}$, etc. mean an element of atomic number Z and atomic mass A.

In a communication (44) dated October 22, 1934, Fermi and his associates reported a great increase in the activation of silver under neutron bombardment when the source of neutrons and the silver were surrounded by quantities of water or paraffin. This was shown to be a specific effect of a substance containing hydrogen, although exhibited to a lesser degree by carbon, iron, lead, and silicon. It was correctly attributed by Fermi to the slowing down of the neutrons by collision with hydrogen nuclei, the resulting slow neutrons having a larger probability of capture than fast neutrons. This phenomenon has proved to be of great importance in the study of nuclear reactions.

During the past year, the investigations in the field of artificial radioactivity have been concerned with the discovery of new radioelements and the collection of data concerning them. Advances in our understanding of the effects due to slow neutrons have also been made, although this subject is by no means closed as yet. The present paper is an attempt to treat in some detail the experimental situation at the end of October, 1935.

II. GENERAL STABILITY CONSIDERATIONS

It has long been a subject of remark that in a diagram whose ordinate is atomic weight, or the difference between atomic weight and atomic number, and whose abscissa is atomic number, the points representing the stable isotopes found in nature and measured in the mass-spectrograph lie in a well-defined region (figure 1). As this can hardly be regarded as being fortuitous, we must consider the stable isotopes as defining a region of stability outside of which lie nuclei which can be formed by the expenditure of energy, but which, once formed, tend to return to the region of stability by one of the three processes: the expulsion of an alpha-particle, the transformation of a nuclear neutron into a proton with the consequent expulsion of a negative electron, or the reverse transformation of a nuclear proton into a neutron, with the emission of a positron. The rules of isotopic statistics (8), particularly those concerning the paucity of isotopes

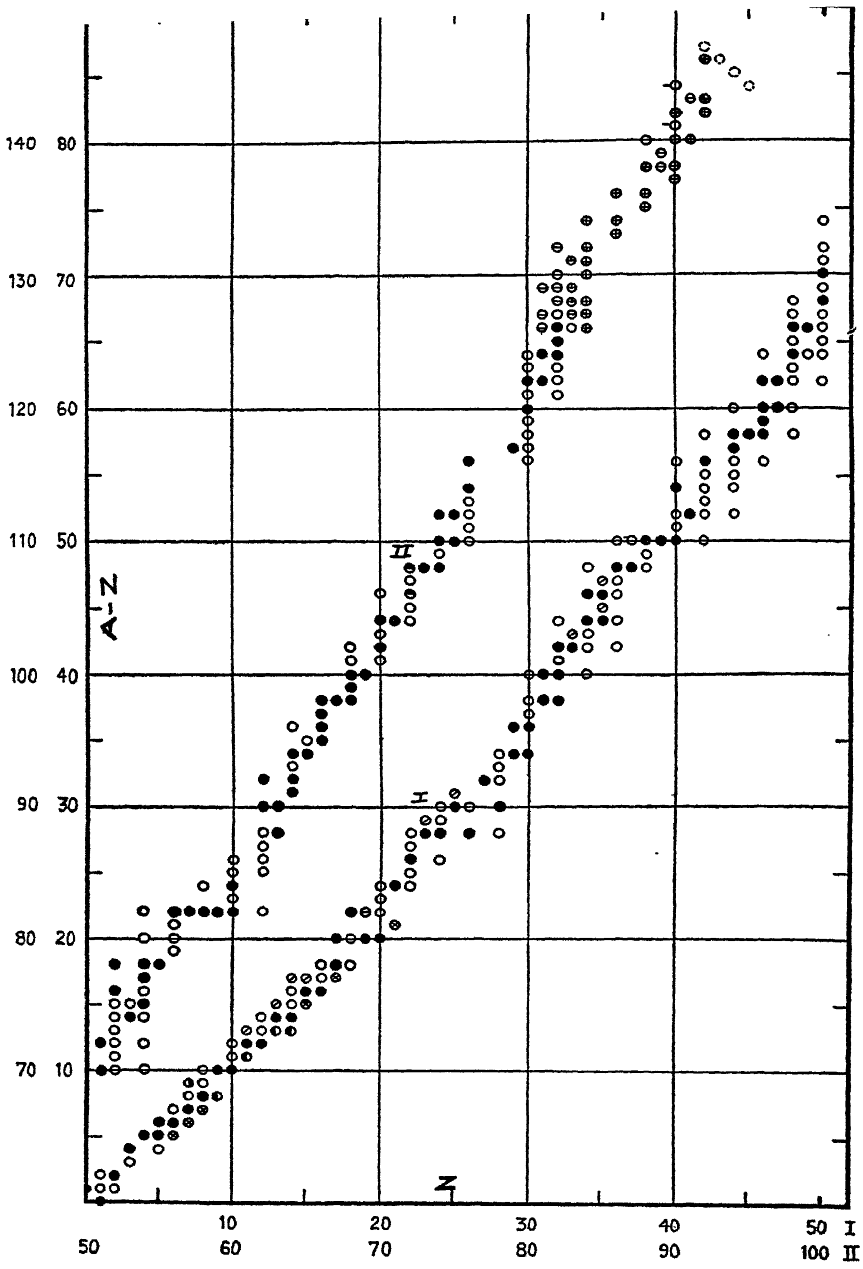

FIG. 1. A plot of the nuclear charge (atomic number), Z, against the atomic mass minus the nuclear charge, $A - Z$, for all the known isotopes. ●, stable isotopes $>$ 20 per cent; ○, stable isotopes $<$ 20 per cent; ⊕, natural α-emitters; ⊖, natural β-emitters; ⦶, artificial β-emitters; ⊗, artificial positron emitters; ◑, artificial positron emitters (?); ◐, artificial positron emitters (?).

with odd atomic number and that of isotopes with odd $A - Z$, where A is mass-number and Z is charge-number, doubtless have an important bearing, whose meaning has not yet been completely elucidated, on the matter of nuclear stability. The problems of stability of nuclei have been examined in detail by many authors; here a brief and completely qualitative discussion will suffice.

In figure 2 the stable isotopes up to chlorine are plotted as circles, and the artificial radioelements in this region of the periodic table are plotted as squares, the arrows indicating their mode of formation. The diagram will be better understood after reference to section III, below, which it is intended to illustrate, but here it should be noted that the stable isotopes lie in extremely regular grouping, and that all of the radioactive isotopes lie in such a position that they can transform themselves into stable isotopes by the emission of a positron or an electron, and that in every case they do emit the appropriate particle. It is also to be noted that those unstable nuclei which lie above and to the left of the line defining the stable isotopes emit electrons to return to the region of stability, while those below and to the right emit positrons, as is indeed demanded by their positions on the diagram. Among the heavier elements are known cases in which the emission either of a positron or of an electron would return the artificial radioelement to a stable form; in all such cases which have been examined, a negative electron is emitted, but it is by no means certain that this is always the case.[4]

III. THE REACTIONS LEADING TO THE FORMATION OF ARTIFICIAL RADIOELEMENTS

There are only eight type-reactions which need be adduced to explain the formation of all (about 100) the artificial radioelements known to date, with one or two possible exceptions which are considered in section IX (paragraphs on indium and bromine). Each reaction has been studied in sufficient detail so that there can be little doubt that it is an established one. It should be always explicitly borne in mind that in all these reactions the conservation of energy in the broad relativistic sense is satisfied, so that in reactions V and VIII, for example, gamma-radiation of the appropriate energy must always be emitted.

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[4] The fact that electrons and positrons are emitted in radioactive processes is not to be regarded as evidence for their existence, as such, in the nucleus. Indeed, it can be shown from quite general considerations that it would not be feasible to try to describe the quantum mechanical behavior of an electron located in a region as small as the nucleus. Accordingly it is more profitable, for the present at least, to consider the nuclei as consisting of the heavier particles such as protons, neutrons, and perhaps alpha-particles.

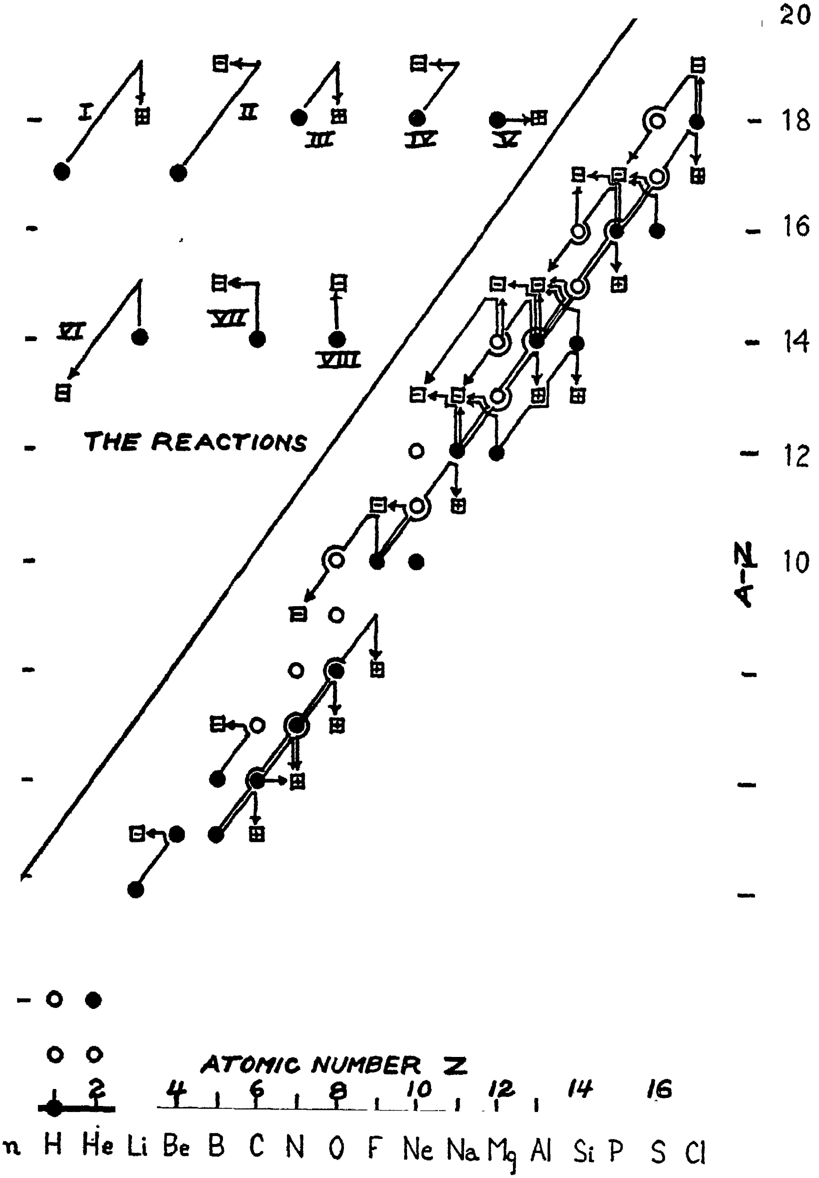

FIG. 2. Artificial radioactivity in the light elements. Z is the atomic number or nuclear charge, and A is the atomic mass. ○, stable isotopes; ●, stable isotopes whose abundance is 20 per cent or greater; □, radioactive isotopes. The sign of the emitted β-particle is shown by + or − in squares.

A. Reactions produced by alpha-particle bombardment

Reaction I. Capture of the alpha-particle with emission of a neutron.

$$_{Z}X^{A} + {}_{2}He^{4} \rightarrow {}_{Z+2}Y^{A+3} + {}_{0}n^{1}, \text{ followed by } {}_{Z+2}Y^{A+3} \rightarrow {}_{Z+1}W^{A+3} + {}_{1}e^{+}$$

This is historically the first reaction of artificial radioactivity, being that observed by Curie and Joliot (26) in the cases of boron and aluminum bombarded by alpha-particles. They thought that this reaction also led to the 2.3-minute period observed in magnesium bombarded with alpha-particles. Although this reaction doubtless does take place, the period of the positron emission is unknown, the 2.3-minute period being due to Al^{28}, formed in accordance with reaction II, below. (See paragraph on magnesium in section IX.)

In all the cases known in which reaction I takes place, the alternative emission of a proton at the moment of alpha-particle capture, leading at once to the stable isotope $_{Z+1}W^{A+3}$, also takes place, with a much greater probability. The successive emission of a neutron and a positron, or the immediate emission of a proton, from an element bombarded with alpha-particles, may be thought of as alternative routes between the two stable isotopes $_{Z}X^{A}$ and $_{Z+1}W^{A+3}$, and the energy expended along either route must be equal to that expended along the other.

Reaction II. Capture of the alpha-particle with emission of a proton.

$$_{Z}X^{A} + {}_{2}He^{4} \rightarrow {}_{Z+1}W^{A+3} + {}_{1}H^{1}, \text{ followed by } {}_{Z+1}W^{A+3} \rightarrow {}_{Z+2}Y^{A+3} + {}_{-1}e^{-}$$

This reaction, which was discussed in the last paragraph for the case in which it gives rise to a stable isotope, sometimes leads to an artificial radioelement. Reaction I is then the alternative one, leading in one step from the stable isotope $_{Z}X^{A}$ to the other stable isotope $_{Z+2}Y^{A+3}$.

B. Reactions produced by deuton bombardment

Reaction III. Capture of the deuton with emission of a neutron.

$$_{Z}X^{A} + {}_{1}H^{2} \rightarrow {}_{Z+1}W^{A+1} + {}_{0}n^{1}, \text{ followed by } {}_{Z+1}W^{A+1} \rightarrow {}_{Z}X^{A+1} + {}_{1}e^{+}$$

This is the earliest known reaction involving deutons. It gives rise in the case of carbon bombarded by deutons to N^{13}, the same radioelement which is produced in boron by alpha-particle bombardment. Reactions III and IV may be regarded as alternative in the same manner that reactions I and II have been so regarded above.

Reaction IV. Capture of the deuton with emission of a proton.

$$_{Z}X^{A} + {}_{1}H^{2} \rightarrow {}_{Z}X^{A+1} + {}_{1}H^{1}, \text{ followed by } {}_{Z}X^{A+1} \rightarrow {}_{Z+1}W^{A+1} + {}_{-1}e^{-}$$

This reaction, first studied by Lawrence (64), gives rise to the same radioelements that are formed by reaction VIII, below. It is noteworthy that even at energies (up to 5 m.e.v.) far below the height of the potential barrier opposed to the entry of the deuton into heavy nuclei, this reaction has a measurable yield in elements as heavy as platinum ($Z = 78$). The theory of the reaction has been given by Oppenheimer and Phillips (81), and is in substantial agreement with the experimental data. Our information concerning the beta-radioactive elements of the shortest half-lives and most energetic electron-spectra known (20, 21) also comes from this reaction.

C. The reaction produced by proton bombardment

Reaction V. Radiative capture of the proton.

$${}_Z X^A + {}_1H^1 \rightarrow {}_{Z+1}W^{A+1} + h\nu, \text{ followed by } {}_{Z+1}W^{A+1} \rightarrow {}_Z X^{A+1} + {}_1e^+$$

There has in the past been considerable confusion in the reports concerning this reaction which have emanated from different laboratories (17, 18, 23, 50). This confusion is to be attributed to the failure to recognize that we have here a case of "resonance" penetration of the target nucleus by the proton, with no third particle to carry off any excesses of energy and momentum. An appreciable yield in the reaction will result only near certain definite "resonance levels," which may be supposed roughly to correspond to quantized states of the proton in the field of the target nucleus.

When the yield of artificial radioactivity is plotted as a function of bombarding particle energy, the time of exposure and bombarding ion current being supposed held constant throughout the measurements, the shape of the curve obtained for a reaction of type V will be very different from the shape of the yield–voltage curve obtained for a reaction such as reaction III, where a neutron is emitted at the instant of formation of the artificial radioelement. In the latter case, the probability of disintegration increases in approximately an exponential fashion with the energy of the bombarding particle, while in the former instance, the probability of disintegration is different from zero only when the energy of the bombarding particle is in the neighborhood of a "resonance" value. If the target under bombardment is thicker than the range of the bombarding particles in the material of which it is composed, then a yield–voltage curve for reaction IV will consist of plateaus separated by abrupt rises in the yield which occur each time the energy of the bombarding particles becomes as high as a "resonance" level. The yield–voltage curve measured in a "thin" target (i.e., a target in which each proton in the ion beam loses only a few thousands of volts energy) will consist of the differential of the thick target curve, namely, a series of peaks, each member of which occurs at a "resonance" value of the energy.

Taken in connection with the differences in voltage scales at different laboratories, the foregoing considerations make it by no means surprising that Cockcroft, Gilbert, and Walton (17, 18) have failed to find the radioactivity produced in boron by proton bombardment, and that Hafstad and Tuve (50) at first failed to find the activity produced in carbon by proton bombardment.

The "resonance" character of reactions of this type will no doubt be very useful in the future in standardizing high-voltage outfits used for nuclear investigations, in the same manner that melting points are useful in establishing a scale of temperatures.

Reaction V has been treated theoretically by Breit and Yost (15).

D. Reactions produced by neutron bombardment

Reaction VI. Capture of the neutron with emission of alpha-particle.

$$_{Z}X^{A} + {}_{0}n^{1} \rightarrow {}_{Z-2}Q^{A-3} + {}_{2}He^{4}, \text{ followed by } {}_{Z-2}Q^{A-3} \rightarrow {}_{Z-1}R^{A-3} + {}_{-1}e^{-}$$

This reaction, where it leads to the formation of an artificial radioelement, is usually endothermic, so that it will take place only when the neutron has a certain minimum energy. There are cases (boron, lithium) in which a stable nucleus is formed in a similar reaction, and here the reactions are exothermic and seem to have a greater probability when the neutrons have almost zero energy (4, 16).

Reaction VII. Capture of the neutron with emission of a proton.

$$_{Z}X^{A} + {}_{0}n^{1} \rightarrow {}_{Z-1}R^{A} + {}_{1}H^{1}, \text{ followed by } {}_{Z-1}R^{A} \rightarrow {}_{Z}X^{A} + {}_{-1}e^{-}$$

This reaction, like VI, involves the emission of a heavy charged particle from the struck nucleus, and hence, as a rule, requires energetic neutrons for its production. It should also be remarked, in connection with reactions VI and VII, that since the emergent heavy charged particle must escape from the attractive field at the center of the nucleus, which becomes stronger with increasing charge-number of the nucleus involved, these reactions are found to take place only among the light elements, viz., those of charge-number less than about 30.

Reaction VIII. Radiative capture of the neutron.

$$_{Z}X^{A} + {}_{0}n^{1} \rightarrow {}_{Z}X^{A+1} + h\nu, \text{ followed by } {}_{Z}X^{A+1} \rightarrow {}_{Z+1}W^{A+1} + {}_{-1}e^{-}$$

This is, to date, the most frequently occurring reaction encountered in the production of artificial radioactivity; indeed, it takes place in a larger number of elements than any other known nuclear reaction. When it was first observed that a radioelement isotopic with its parent could be formed by neutron bombardment, there were theoretical difficulties in accepting the idea of simple capture of a neutron of several millions of volts energy by a stationary nucleus, without the emission of any heavy particles whatever. Incontrovertible evidence that the radioelement formed was in fact the next heavier isotope of the bombarded element made it clear that capture of the neutron was indeed occurring, while the discovery, already mentioned in section I, that the slowing-down of neutrons by a substance containing hydrogen greatly enhanced the probability of this reaction, made it seem likely that the energy of the neutrons entering the reaction is always very low. The activity due to this reaction which is observed in the absence of any hydrogen-containing substance surrounding the source of neutrons and target being activated may then be attributed to the neutrons of low energy produced by scattering from nearby objects of the neutrons emitted by the source.

A theoretical treatment of the reaction, made along substantially the same lines and offered about the same time by Bethe (10), Perrin and Elsasser (84), and Fermi (4), seems to have several features that are not in accord with the experimental results.

Reaction VIII is by no means limited to cases in which the product nucleus is unstable, as is shown by the enormous absorption for slow neutrons displayed by such substances as cadmium, mercury, and gadolinium, which are only feebly activated by neutron bombardment. In such cases, the next heavier isotope of cadmium, mercury, gadolinium, etc. is stable and is formed by the radiative capture of the neutron.[5] Gamma-rays emitted in such neutron capture, in the production of both stable and unstable nuclei, have been observed by Fermi (4) and others (45, 61). Their energy has been roughly measured in several cases by Rasetti (86).

It should be remembered that, while the emission of gamma-rays is demanded in reactions V and VIII, it may also occur for any of the other reactions. Until such gamma-rays have been sought and their energy determined, if they exist, it will not be possible unambiguously to balance mass and energy in any of the reactions just discussed. In attempting to strike such a balance, one should bear in mind that the tabulated isotopic masses ordinarily met are *atomic* masses, and hence include the masses of all the extranuclear electrons. The reason for this seems to be that one of the original purposes of isotopic mass determinations was to enable their comparison with atomic weights measured by the chemists. Now that the chief usefulness of isotopic masses is in balancing the equations of nuclear reactions, it would seem that the masses of the extranuclear electrons might well be subtracted. If one uses a table of *atomic* masses in calculating the energy balance in a reaction in which an electron is emitted, the mass of the emitted electrons should not be taken into account in the computation, for its loss from the radioactive atom is compensated by the gain of a new extranuclear electron demanded by the fact that the charge-number of the nucleus has been raised by one, owing to the loss of the disintegration electron. In the case of positron emission, on the other hand, *twice* the electron rest-mass energy should be added to the energy of disintegration, for not only has the positron escaped, but an extranuclear electron will be lost owing to the reduction of the nuclear charge-number by one unit.

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[5] For example, the known isotopes of cadmium are 106, 108, 110, 111, 112, 113, 114, 115, 116, and since the abundant ones differ by unity, any isotope formed by neutron capture would be one of these and therefore stable. The isotopes 106, 108, and 116 are present in only small amounts in cadmium.

It seems clear from the investigations of Henderson (55) and of Crane, Delsasso, Fowler, and Lauritsen (20), that the maximum energy of the continuous beta-particle spectrum, and not the mean energy, should be taken as the energy of electron or positron disintegration.[6]

IV. CHEMICAL IDENTIFICATION OF THE RADIOACTIVE ISOTOPES

Until the discovery of artificial radioactivity, the end-products of nuclear disintegrations were identified only by inferences involving the number and character of particles known to be emitted in the reactions, and the balance of energy in the nuclear reaction postulated to explain the disintegration. The probabilities of the known nuclear disintegrations range from about 10^{-6} to 10^{-11} per incident bombarding particle, and although in an ion-accelerating tube currents of 10^{13} ions per second are by no means unusual, it is immediately obvious that the bombardment time required to make a spectroscopically detectable amount of the product of the most favorable nuclear reaction is impossibly long. The same argument applies to any other means of detecting a gross amount of a stable isotope which may be formed in a nuclear disintegration.

If the product of the reaction is radioactive, however, the situation is entirely changed, for extremely sensitive methods of detection of charged particles in rapid motion are available. By the use of a Geiger counter or a sensitive electroscope, the detection of 10^5 or 10^6 sufficiently radioactive atoms is very easy. Since the chemical character of an atom is determined by the charge on its nucleus, without regard to the structural stability of that nucleus, it is clear that the moment a disintegration leading to the formation of a new and unstable nucleus takes place, the newly-born atom has properties determined by its new charge-number and will behave in all chemical respects like the element of which it is an isotope.

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[6] The fact that the energy spectrum of the beta-particles of a beta-active substance is continuous, and not discrete, has led to the assumption of the existence of the neutrino, a particle of small mass and no charge, introduced to preserve the conservation laws of momentum and energy in beta-ray decay.

The chemical identification of artificial radioelements is based on the fact that isotopes are not appreciably separated by ordinary chemical reactions. Thus, if an element consists of the fraction A of isotope a, and $(1 - A)$ of isotope b, and if the fraction B of the total enters into a chemical reaction, then AB and $B(1 - A)$ will be the fractions of each isotope that have reacted. While the chemical behavior of the few hundreds of thousands or few millions of atoms of an artificial radioelement formed in a nuclear reaction may be erratic and uncertain, if a quantity of that element with which the radioelement is suspected of being isotopic is added, and then completely separated out chemically and examined for activity, it can be definitely established whether or not the radioelement is isotopic with the element in question; for, if the isotopy exists, all of the radioactivity will have been separated out in the removal of the element under examination.

It must be pointed out that failure to separate a radioelement from an added element is not sufficient evidence for the statement that they are isotopic with each other. Also, isotopes may be separated from each other chemically, if they exist in different valence states. If, after a chemical treatment calculated to bring both the radioelement and the known added element to the same valence state, a separation can be effected, one has reasonably good proof that the two are not isotopic. The fact that two elements coprecipitate or are carried along together in some reactions does not establish that they are isotopic, as all chemists know well.

When the artificial radioelement produced in a nuclear reaction is an isotope of a completely unknown element, or of one so rare or itself so radioactive that none can be added to the radioelement to stabilize its chemical properties, the matter of chemical identification becomes a great deal more difficult. Such a case occurs in the bombardment of uranium by neutrons: Fermi, who first studied this reaction, early concluded (42) that at least one of the half-lives observed belonged to an element of charge-number 93, for its chemical properties did not seem to be those of any of the known elements from 86 to 92 inclusive. This point of view was criticized by von Grosse and Agruss (49), who thought that the experiments of Fermi did not exclude the possibility that the radioelement in question might be isotopic with element 91, whose isotopes occurring in nature—protactinium and UX_2—are both very rare. New experiments by Fermi (4) and Hahn and Meitner (52) seemed to indicate that not only element 93, but also elements 94 and 95 were formed in the bombardment of uranium by neutrons, a chain of radioactive products apparently being initiated. Interesting results have been obtained also in the bombardment of thorium by neutrons, and our knowledge of the effects of neutron bombardment of the naturally radioactive elements, sketchy as yet (see section IX, where the reactions for each element are treated in detail), may be expected to shed some light on the problems of the uranium, thorium, and actinium series, and perhaps on the missing elements 85 and 87.

For many years the use of the naturally radioactive elements as indicators in chemical reactions involving their stable isotopes has been a well-known technique (82) in chemistry, although it is one drastically limited in scope by the fact that (except for the cases, unimportant in this connection, of potassium, rubidium, and samarium) the naturally radioactive elements are restricted to the atomic numbers 81 to 92, inclusive. The ready availability of radioactive isotopes of almost all the stable elements (see section IX) should make possible many experiments not feasible in any other way in which these radioelements are used as indicators. The application to biochemical studies is also worthy of consideration.

V. CONCENTRATION OF THE ARTIFICIAL RADIOELEMENTS

It is evident that if the radioelement produced in a nuclear reaction is not isotopic with the bombarded element, a very effective concentration of the radioactivity can be performed by separating out the active element by means of an appropriate chemical reaction, a few milligrams of the element with which the radioelement is isotopic having been added to stabilize the chemical behavior of the small number of active atoms. This self-evident procedure has often been employed.

Another method of concentrating a radioelement differing chemically from its parent, which has a much more limited range of application, was that of electrochemical deposition. This has been employed by Haissinsky (54) in the concentration of radiocopper, produced by neutron bombardment of zinc. In order that this means may be applicable, the radioelement must be electrochemically more noble than its parent.

In the case which has occurred most frequently to date in the production of artificial radioelements—that in which the radioactive element is isotopic with its parent—the situation is by no means so hopeless as is the chemical separation of ordinary isotopes. Szilard and Chalmers (94) first showed that active iodine could be separated from ordinary iodine by making use of the fact that when I^{128} is formed by the capture of a neutron by I^{127}, the new nucleus is likely to be removed from its chemical bond in the compound of iodine being irradiated, either by the kinetic energy of the captured neutron or, if this energy is too low, by the recoil produced by the gamma-ray whose emission is demanded according to reaction VIII. Whether the atom freed in this way will interchange with its isotopic atoms bound in the irradiated chemical compound will depend on the nature of the chemical compound dealt with. To prevent such interchange, Szilard and Chalmers worked with non-ionizing organic compounds, such as ethyl iodide and bromoform, with a trace of free halogen added to protect the radioactive isotope. After the irradiation the free iodine or bromine was reduced and precipitated as a silver halide, which proved to contain almost all of the activity.

Fermi (4) has prevented the interchange of radioactive and ordinary chlorine atoms by irradiating a compound in which the chlorine is bound in a radical which, once destroyed, has a negligible probability of being rebuilt. If sodium chlorate is irradiated, a trace of chloride ion added, and silver chloride precipitated, from 70 to 90 per cent of the activity is concentrated in the precipitate. Care must be taken to prevent the precipitation of silver chlorate. Similar results can be obtained with bromates and iodates. Manganese dioxide precipitated from irradiated potassium permanganate carries a large part of the activity due to radiomanganese.

Physical methods of separation depend on the fact that the atom is likely to have lost one or more extranuclear electrons at the moment of formation, owing to the energy imparted to it either by the captured neutron or the emitted gamma-ray. Hence the net electric charge on the atom permits its collection by an electrostatic field. Such methods have been employed by Fermi (4) and by Paneth (83) for the concentration of radioactive isotopes of the bombarded element.

The phenomenon of recoil of the struck nucleus at the moment of formation of an artificially radioactive nucleus was first observed by Wertenstein (96), in the case of radiofluorine formed from atmospheric nitrogen by alpha-particle bombardment, and has since been observed in many cases in which a heavy particle is either captured or emitted in the formation of an artificial radioelement (17, 18, 67).

The possibility of concentrating an artificial radioelement makes artificial radioactivity useful as a detector of neutrons, which can be obtained only in the presence of gamma-radiation so intense that electrical methods of detection are not feasible.

VI. REACTIONS INVOLVING SLOW NEUTRONS

No treatment of artificial radioactivity would be complete if it did not include a discussion of the effects due to "slow" neutrons. In October, 1934, Fermi and his coworkers (4) found that the activation of silver by the neutrons from a radon–beryllium source could be increased several fold by surrounding source and detector by large quantities of water or paraffin. The effect was shown to be specifically due to the hydrogen content of the water or paraffin. The most obvious explanation for the phenomenon was that the neutrons from the source, initially having all energies from 0 to about 7 m.e.v. (31), lost energy in collisions with the hydrogen nuclei present in the water or paraffin, and that these slowed-down neutrons were much more effective in producing radioactivity in silver than were the neutrons of higher velocities. When the effect of substituting such materials as silica and iron for the paraffin and water was examined, it was found that a small increase in the activation was produced by surrounding the source and detector with these materials, but the magnitude of the effect was not comparable with that attained by the disposition of large masses of paraffin about the source during irradiation. This lent added weight to the hypothesis that the slowing-down of the neutrons is responsible for the observed effect, as a neutron can lose more energy in a collision with a nucleus of hydrogen than in one with a heavier nucleus. When other detectors were substituted for the silver, the striking discovery was made that all the reactions of type VIII, and only these reactions, showed an enhancement when the neutrons were slowed down.

The assumption was early made by Fermi (4) that the energies of the neutrons conventionally called "slow" were of the order of magnitude of thermal energies of agitation, that is, about 1/40 of a volt. It can be shown that the impact of a neutron against a proton reduces the energy of the neutron, on the average, by a factor of $\frac{1}{2}$. From this it follows that in the course of fifteen impacts the energy of a neutron is reduced to about 1/30,000 of its original value. With a neutron of initial energy 4 m.e.v., less than thirty impacts would be necessary to reduce the energy to thermal values. Experiments designed to measure the energy of slow neutrons will be discussed in section VIII.

The intense activation observed in many elements bombarded with slow neutrons suggests that the absorption of slow neutrons in these elements must be correspondingly large. This proved to be the case, but the discovery was also made (4) that many elements which did not show pronounced radioactivity under neutron bombardment exhibited an extremely large absorption for slow neutrons. In the cases of heavier elements (cadmium, mercury, and others), this is to be attributed to the radiative capture of a slow neutron, in complete accordance with reaction VIII, except that the nucleus formed by neutron capture is in these cases a stable isotope of the bombarded element, so that no radioactivity is observable. The energy of the gamma-rays emitted in the capture of a neutron of nearly zero kinetic energy can be estimated from the fact that Aston (8) has found the mass difference between neighboring isotopes of the same element to be always approximately unity in the region of the periodic table where this phenomenon of large slow neutron absorption without consequent radioactivity occurs. The mass of the neutron (9) is fairly accurately known to be 1.0085 on the "physical" scale of masses ($O^{16} = 16$), so that when a free neutron is captured and bound in a nucleus about 7.5 m.e.v. of energy must be radiated. The measurements of Rasetti indicate that the energy of the capture radiation is in some cases as small as about 4 m.e.v., so that the possibility must be admitted that there is emission of more than one quantum per capture process, i.e., that the radiation of the 7.5 m.e.v. takes place in two or more steps.

In his studies of the absorption of slow neutrons, Fermi (4) further found that certain light elements (boron and lithium) exhibited large absorption for the slow neutrons, without becoming radioactive and also without emitting gamma-radiation at the moment of neutron capture. This has been shown to be due to the capture of the neutron in the boron or lithium nucleus, and the subsequent disintegration of the product nucleus with the emission of heavy particles (16). This latter phenomenon (viz., the emission of heavy particles) may be regarded as an alternative to the emission of gamma-radiation at the moment of neutron capture; the energy balance in the reaction can be preserved in either way.

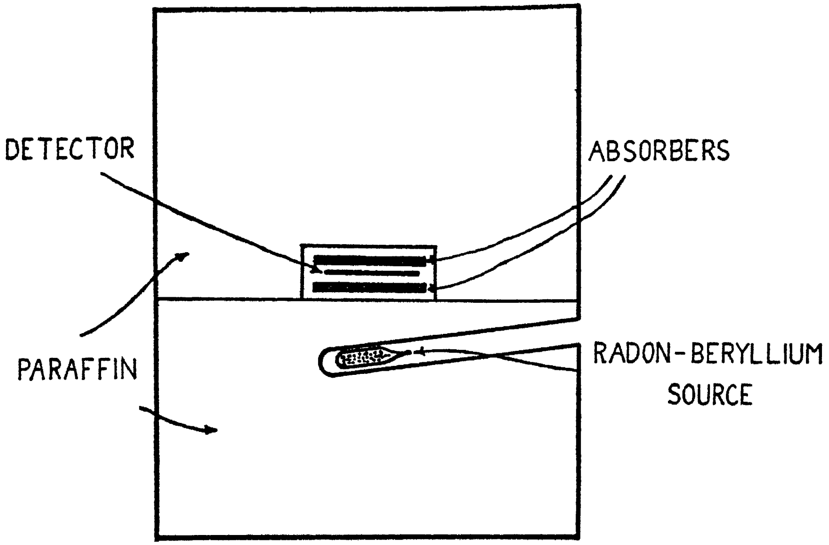

FIG. 3. Fermi's arrangement for measuring absorption of slow neutrons

VII. ABSORPTION OF SLOW NEUTRONS

The earliest measurements of the absorption of slow neutrons were made by Fermi (4), with the experimental arrangement shown in figure 3. The absorption curves he obtained with this arrangement were not exponentials, as indeed the geometry would lead one to expect, even though the absorption measured in a parallel beam might follow an exponential law.[7] Experimental evidence that this is indeed the case has been obtained for absorption in cadmium by Dunning (33) and Ehrenberg and Hu Chien Shan (37), and for absorption in silver by the latter investigators. Fermi used for the detection of the neutrons transmitted through his absorber the radioactivity induced by these neutrons in a sheet of rhodium or of silver.

Another method of slow neutron detection is to count the heavy particles emitted in the disintegration of lithium by slow neutrons. The reaction, mentioned in the last section, is

$${}_3\mathrm{Li}^6 + {}_0\mathrm{n}^1 \rightarrow {}_2\mathrm{He}^4 + {}_1\mathrm{H}^3$$

the alpha-particles having a range of about 6 mm. and the ${}_1\mathrm{H}^3$ a range of 15 mm. It is not difficult to count the individual particles produced in this reaction by one of the electrical counting procedures customary for the measurement of alpha-particles from naturally radioactive sources. Dunning and his coworkers (33) have made extensive measurements of the absorption of slow neutrons in various substances, detecting by means of a "linear" amplifier (32) the heavy particles emitted in the lithium reaction. The geometrical arrangement of his source, absorbers, and detector is shown in figure 4, which demonstrates that his absorption measurements were made on a beam of slow neutrons much more nearly parallel than that used by Fermi.

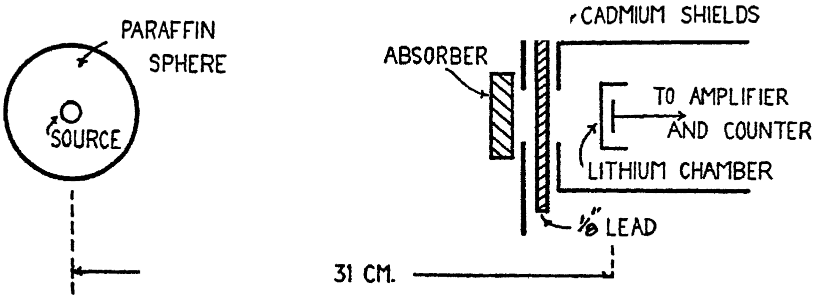

FIG. 4. Dunning's arrangement for measuring the absorption of slow neutrons

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[7] A simple geometrical calculation shows that if the assumptions are made that (a) the absorption of neutrons from a parallel beam is strictly exponential and (b) that the distribution of neutrons in the paraffin is sensibly uniform (which is usually the case), the fraction of neutrons transmitted through an absorber of thickness d is

$$e^{-k} - ke^{-k} - k^2Ei\ (-k)$$

where $k = \sigma Nd$, σ is the cross section for absorption, and N is the number of nuclei per cubic centimeter in the absorber.

TABLE 1

Neutron-nucleus collision cross sections

ELEMENT	ATOMIC NO.	ATOMIC WT.	COMPOUND USED	GRAMS PER SQ. CM.	FRACTION TRANSMITTED	CROSS SECTION × 10^{24}, SQ. CM.	
						Slow	Fast
H	1	1.008	$(CH_2)_n$	0.131	0.673	55	1.68
D	1	2.014	D_2O	1.36	0.631	4.0	1.71
Li	3	6.94	LiF	0.24	0.765	45	1.84
Be	4	9.02	Be	0.703	0.780	5.3	1.65
B	5	10.82	B_4C	0.0557	0.418	360	1.60
C	6	12.00	C	2.86	0.549	4.1	1.65
N	7	14.01	NaN_3	1.30	0.630	11.3	1.76
O	8	16.00	SiO_2	3.78	0.709	3.3	
F	9	19.00	NaF	1.94	0.827	2.5	
Na	11	23.00	Na	1.48	0.847	4.2	
Mg	12	24.32	Mg	4.67	0.669	3.5	
Al	13	26.97	Al	7.24	0.788	1.5	2.4
Si	14	28.06	Si	2.23	0.867	2.5	
P	15	31.03	P	1.69	0.615	14.7	
S	16	32.06	S	6.6	0.840	1.4	2.6
Cl	17	35.46	NaCl	1.35	0.541	39	
K	19	39.10	K	1.60	0.816	8.2	
Ca	20	40.07	CaO	1.87	0.751	11.0	
Ti	22	48.1	TiO_2	1.97	0.760	11.9	
V	23	50.96	V_2O_5	2.41	0.751	10	
Cr	24	52.01	Cr	5.82	0.718	4.9	
Mn	25	54.93	Mn	3.69	0.558	14.3	
Fe	26	55.84	Fe	3.87	0.605	12.0	3.0
Co	27	58.94	Co	1.41	0.602	35	
Ni	28	58.69	Ni	3.03	0.637	15.4	
Cu	29	63.57	Cu	6.22	0.642	7.5	3.2
Zn	30	65.38	Zn	10.7	0.627	4.7	3.3
Ge	32	72.60	GeO_2	0.08	0.93	75*	
As	33	74.96	As	5.28	0.692	8.6	
Se	34	79.2	Se	3.47	0.606	19	
Br	35	79.92	KBr	3.43	0.705	11.9	
Sr	38	87.63	$SrCrO_4$	2.21	0.832	9*	
Y	39	88.9	Y_2O_3	0.18	0.463	800	
Zr	40	91	ZrO_2	1.87	0.807	16.7	
Cb	41	93.1	Cb_2O_5	1.01	0.90	14*	
Mo	42	96.0	Mo	1.70	0.926	7.1	
Ru	44	101.7	Ru	6.1	0.647	12.5	
Rh	45	102.9	Rh	0.62	0.664	115	
Pd	46	106.7	Pd	6.2	0.715	10−	
Ag	47	107.88	Ag	1.88	0.557	55	
Cd	48	112.41	Cd	0.0416	0.524	3300	
Sn	50	118.70	Sn	18.8	0.678	4.0	4.3

TABLE 1—*Concluded*

ELEMENT	ATOMIC NO.	ATOMIC WT.	COMPOUND USED	GRAMS PER SQ. CM.	FRACTION TRANSMITTED	CROSS SECTION $\times 10^{24}$, SQ. CM.	
						Slow	Fast
Sb	51	121.77	Sb	7.26	0.745	8.1	
Te	52	127.5	Te	5.52	0.790	8.2	
I	53	126.93	I	6.78	0.738	9.4	4.6
Ba	56	137.37	BaO	0.662	0.680	140	
La	57	138.90	La_2O_3	0.214	0.933	80	
Ce	58	140.25	CeO_2	0.98	0.896	25*	
Pr	59	140.9	Pr_2O_3	2.43	0.77	25	
Nd	60	144.27	Nd_2O_3	0.72	0.559	220	
Sm	62	150.43	Sm_2O_3	0.04	0.525	4700	
Eu	63	152	Eu-Gd-Al	0.02	0.647	1000*	
Gd	64	157.6	Gd_2O_3	0.0068	0.590	30,000	
Tb	65	159.2	Tb-Al	0.06	0.919	1000*	
Dy	66	162.5	Dy-Al	0.27	0.685	700	
Ho	67	163.4	Ho-Al	0.144	0.877	400*	
Er	68	167.7	Er_2O_3	0.666	0.780	120	
Tm	69	169.4	Tm-Al	0.07	0.987	500*	
Yb	70	173.6	Yb_2O_3	0.315	0.912	90	
Lu	71	175.0	Lu-Al	0.045	0.93	400*	
Ta	73	181.5	Ta	4.56	0.663	27	
W	74	184.0	W	7.05	0.592	23	5.3
Re	75	186.31	Re	2.39	0.501	89	
Os	76	190.6	Os	5.35	0.643	27	
Ir	77	193.1	Ir	0.785	0.509	285	
Pt	78	195.2	Pt	4.30	0.769	25	
Au	79	197.2	Au	2.52	0.508	88	
Hg	80	200.61	HgO	0.545	0.556	380	5.8
Tl	81	204.39	Tl	10.5	0.710	11	
Pb	82	207.20	Pb	22.7	0.568	8.6	5.7
Bi	83	209.00	Bi	9.07	0.805	8.2	
Th	90	232.15	ThO_2	2.75	0.772	32	
U	92	238.17	UO_2	2.52	0.83	43	

* Estimated.

Table 1 is taken from Dunning's paper and gives the cross sections for slow and fast neutron absorption of most of the elements. The cross section σ is defined in the usual way: if a fraction A of the incident number of neutrons is transmitted through a thickness x of absorber, which contains N nuclei per cubic centimeter, then

$$A = e^{-N\sigma x}$$

It will be noted that while for many elements the cross section for slow neutron absorption does not differ appreciably from that for absorption of fast neutrons, in some cases the former is enormously larger than the latter. While the cross section for fast neutron absorption increases monotonically from boron to lead in a way that is not much different from that in which the nuclear radius is supposed to increase, the cross section for the absorption of slow neutrons varies erratically and unpredictably from one element to the next. The cross section of gadolinium, for example, is about 3×10^{-20} sq. cm., leading to a collision radius of about the size of the K shell of electrons.

Since the detection of slow neutrons is always accomplished by means of a reaction that they produce (viz., either capture of the neutron with subsequent radioactivity of the detector, or disintegration of the nuclei of the detector with the emission of heavy charged particles), it seems likely that the measured absorption of an element for slow neutrons might depend on the particular reaction employed in the detection of the neutrons transmitted through a sample of the absorber. That this is indeed the case has been shown experimentally by Moon and Tillman (78) and by Ridenour and Yost (87). Indications of the same effect have also been obtained in connection with other experiments by Bjerge and Westcott (12) and by Artsimovitch and others (7).

It will be seen from the diagrams of the arrangements used by Fermi and by Dunning for absorption measurements (figures 3 and 4), that the effects of neutron capture and of elastic scattering are not separately evaluated; what is measured is simply the efficacy of an absorber in removing slow neutrons from a beam. It is predicted by the theory of Bethe (10) mentioned above (section III), that elements displaying large cross sections for neutron capture will also present large cross sections for elastic scattering of the slow neutrons. This is apparently in complete disagreement with the available experimental facts. Dunning (33) has shown that there is no appreciable elastic scattering from cadmium, Ridenour and Yost (87) have demonstrated that the same is true of silver, and Mitchell and Murphy (77) have found the same result in mercury. Cadmium, silver, and mercury all have large capture cross sections, and should therefore exhibit large elastic scattering, according to the theory. It is possible that elastic scattering may be an important phenomenon in some of the elements, perhaps in some cases more important than capture, but there is at present no experimental evidence that this is the case.

VIII. THE VELOCITY OF THE SLOW NEUTRONS

It is, of course, a matter of the first importance to know definitely in what velocity range the neutrons conventionally called "slow" lie. Slow neutrons may be thought of as those which are strongly absorbed by cadmium, for definiteness, and it has been shown by Dunning (33) that these neutrons are not detectable by counting with a linear amplifier the protons knocked on by them (the usual technique for detecting fast neutrons); while Bonner and Brubaker (13) have demonstrated that the recoil protons due to slow neutrons cannot be observed in a cloud chamber (another standard technique for fast neutron measurement). This sets an upper limit of about 50 to 100 electron kilovolts to the energy of the slow neutrons.

If, as was early supposed by Fermi, the energy of the slow neutrons is that of thermal agitation at room temperature (about 1/40 of a volt) it should be possible to detect a difference in their properties when the medium in which they are slowed down—paraffin or water—is cooled to a much lower temperature, say that of liquid air. The neutrons, being at least partially in thermal equilibrium with their surroundings, should have a different energy distribution in the two cases, and hence a different likelihood of capture. After inconclusive temperature-effect experiments had been performed by Fermi (4) and McLennan and others (72), the first positive evidence of such an effect was presented by Dunning and others (33, 34), who found that the absorption of "cold" (90°K.) neutrons in cadmium was about 4 per cent greater than that of "warm" (273°K.) neutrons. A much larger effect of temperature[8] has been announced by Moon and Tillman (78) and confirmed in part by Fermi (5). The activation of silver, rhodium, and iodine by the neutrons from a radon–beryllium source was found by the former investigators to increase by about 10 to 20 per cent when a layer of paraffin 2.5 cm. thick surrounding the detector was cooled from room temperature to liquid air temperature. The temperature of the neutron source remained constant at that of the room.

More satisfactory than any of these temperature-effect experiments is the result recently announced by Dunning and others (35) for an experiment with a Stern type mechanical velocity selector designed to measure directly and unambiguously the speed of the slow neutrons. In this experiment, four duralumin disks were provided with sectors of sheet cadmium, the sectors subtending 3.7°, the spacing between the sectors being 3.5°. Two of these disks were mounted 54 cm. apart on a shaft which could be rotated, the other two disks being fixed 5 mm. from the rotating ones (figure 5). Since the cadmium is opaque to the slow neutrons and the duralumin transparent, the arrangement forms a velocity selector for the slow neutrons. The results obtained are shown in figure 6, and constitute the most reliable evidence obtained to date that many of the slow neutrons really have thermal velocities.

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[8] Lukirsky and Zavewa (68) show that a temperature effect of as high as 45 per cent is attainable. That is, for silver the activity at liquid air temperatures is 45 per cent greater than that at room temperature. In these experiments the cooled paraffin was 0.8 cm. thick.

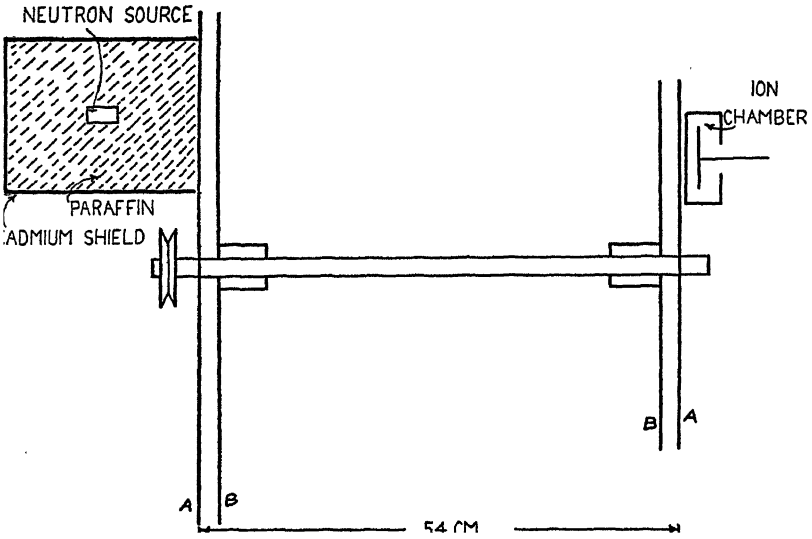

FIG. 5. Schematic drawing of mechanical velocity selector for slow neutrons. A, rotating disk with cadmium sectors; B, fixed disk with cadmium sectors.

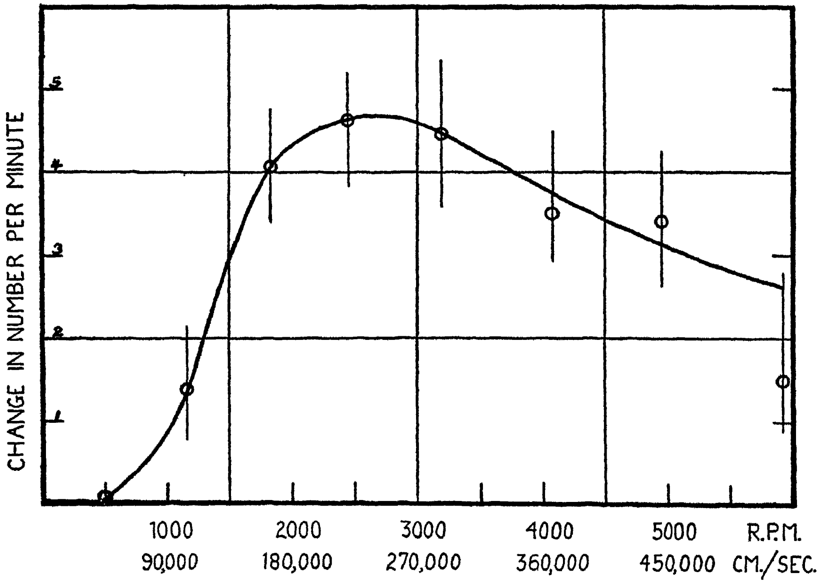

FIG. 6. Curve showing change (decrease) in number of slow neutrons detected after passing through the two shutter systems, as the speed of the sectors was changed. The speed of the sectors is given in revolutions per minute, and the neutron velocity for which the selector is most effective is also indicated.

IX. DETAILED DISCUSSION OF THE ARTIFICIAL RADIOELEMENTS

In this section the reactions producing artificial radioactivity have been treated for the case of each element. The listing is made according to the bombarded element, although it must be noted that in many cases the same artificial radioelement can be made in a variety of ways; for example, Al^{28} is produced from Mg^{25} by reaction II, from Al^{27} by reaction IV or reaction VIII, from P^{31} by reaction VI, or from Si^{28} by reaction VII. The number of the reaction-type which is probably the one responsible for the formation of the radioelement being discussed will be found in the margin to the left of the discussion. The sign of the disintegration electron emitted from each radioelement, where it is not explicitly stated, can be determined from the type of nuclear reaction involved; we have seen in section III that reactions I, III, and V lead to radioelements which emit positrons in their decay, while reactions II, IV, VI, VII, and VIII give electron-emitting isotopes. No case is known in which bombardment by neutrons produces a radioactive emission of positrons. At the end of the paragraph on each reaction is a list of references to the work bearing on that particular reaction; the most important ones are usually mentioned specifically in the paragraph.

The half-value thickness for the absorption of the beta-radiation emitted by an artificial radioelement is often given below in grams per square centimeter of aluminum; the mean energy of the electron or positron spectrum can be obtained very roughly in m.e.v. by multiplying the half-value thickness by 8.

1. Hydrogen

No artificial radioactivity has been excited in this element by neutron, proton, deuton, or alpha-particle bombardment.

2. Helium

The technical difficulties of irradiating and testing for subsequent activity sufficiently large volumes of the noble gases (66) have prevented their careful investigation for artificial radioactivity.

3. Lithium

I? Meitner (75) reported observing the radioactive emission of positrons from lithium bombarded with alpha-particles. The upper energy limit was 0.3 m.e.v., and the half-life several minutes. These she attributed to B^9. She
II? also reports a beta-particle emission of energy and half-life not stated. This was attributed to Be^{10}. This work has not been confirmed.

IV Crane, Delsasso, Fowler, and Lauritsen (21) have found a beta-activity in lithium bombarded with deutons. The half-life is about 0.5 second, and the upper limit of the electron energy spectrum about 10 m.e.v. The activity is probably to be attributed to Li^8 and possibly to H^4. Strong bombardment of lithium with neutrons (4, 43) has yielded no detectable activation, although one might expect the same Li^8 mentioned above to be formed in reaction VIII.

4. Beryllium

An extremely weak activity probably due to impurities was exhibited by beryllium after strong irradiation with slow neutrons (4).

5. Boron

I The formation of N^{13} by alpha-particle bombardment of boron is one of the three reactions by which artificial radioactivity was first discovered. The half-life first measured by Curie and Joliot (26) and Ellis and Henderson (38) was wrong, being given as 14 minutes instead of about 10.5. More accurate measurements by Ellis and Henderson (39) cleared up the consequent difficulty regarding the identity of the N^{13} formed by bombarding boron with alpha-particles, with that formed by bombarding carbon with deutons or protons; N^{13} emits positrons, the upper limit of whose energy spectrum is about 1.3 m.e.v. (References 2, 27, 40.)

IV Emission of electrons from boron following deuton bombardment has been observed by Crane, Delsasso, Fowler, and Lauritsen (20). The half-life is about 0.02 second, and the upper limit of the energy spectrum in the neighborhood of 11 m.e.v. The activity is presumed to be due to B^{12}.

III Crane and Lauritsen (22, 24) and Cockcroft (17, 18) have reported a positron activity with a half-life of 20 minutes, produced by the deuton bombardment of boron. The radioelement involved was shown to be C^{11} by Yost, Ridenour, and Shinohara (97). The upper limit of the positron spectrum is about 1.3 m.e.v., according to Neddermeyer and Anderson (79).

V Crane and Lauritsen (23) found that C^{11} could also be formed in boron by proton bombardment. The reason for Cockcroft's (17, 18) disagreement with this finding has been discussed in section IV.

6. Carbon

III Crane and Lauritsen (22, 24), Cockcroft, Gilbert, and Walton (17, 18), and Henderson, Livingston, and Lawrence (56) have found a positron activity of about 10.1 minutes half-life in carbon bombarded by deutons. Yost, Ridenour, and Shinohara (97) showed that the radioelement was N^{13}.

V Lauritsen and Crane (23) found that the same element was formed in the bombardment of carbon by protons, as had Cockcroft, Gilbert, and Walton (17, 18, 19) and Henderson, Livingston, and Lawrence (56). Hafstad and Tuve (50) could not at first find evidence of such activity, but the discrepancy has been cleared up, and Hafstad and Tuve (51) have now made the best measurements of the voltage excitation function for this resonance reaction. The radiative capture of protons by carbon has been treated theoretically by Breit and Yost (15).

7. Nitrogen

I The phenomenon of recoil of active nuclei formed by alpha-particle bombardment of atmospheric nitrogen, leading to a slight radioactive emission of positrons in all targets when bombarded by alpha-particles in air, was first interpreted correctly by Wertenstein (96) as being due to the formation probably of F^{17} according to reaction I. The half-life is 1.1 minutes. Ellis and Henderson (38) have also studied this radioelement. (References 29, 40.)

III Livingston and McMillan (67) have observed the collection by recoil on to a platinum target bombarded by deutons in air of a radioelement whose parent is nitrogen. This radioelement emits positrons with a half-life of 126 seconds, and has been chemically shown to be oxygen; it is no doubt O^{15}. The upper limit of the positron energy spectrum is 1.7 m.e.v.

8. Oxygen

No radioelement has been formed from oxygen by bombardment with alpha-particles, protons, deutons, or neutrons.

9. Fluorine

I Frisch (48) has recently reported that a positron emission first observed by Meitner (75) from fluorine bombarded with alpha-particles corresponds to the formation of Na^{22}, whose half-life is extremely long,—of the order of six months. The half-value thickness for the positrons is 0.03 g. per square centimeter of aluminum. A chemical separation of the active sodium has been made.

IV Crane, Delsasso, Fowler, and Lauritsen (21) have observed the formation of F^{20} in the bombardment of fluorine with deutons. The upper limit of the electron spectrum is about 5 m.e.v., and the half-life 12 seconds.

I Fermi and coworkers (4, 43) have observed a 9-second and a 40-second activity in fluorine bombarded with neutrons. Neither is sensitive to hydrogen. Both emit negative electrons. Neither can be identified with certainty; one is probably N^{16}, but the identity of the other radioelement is at present obscure. (References 11, 57.)

11. Sodium

I Frisch (47) has observed a positron emission with a half-life of 7 seconds, produced in sodium by alpha-particle bombardment. It is doubtless to be attributed to Al^{26}. The upper spectral limit is about 1.8 m.e.v.

IV Lawrence (64) has produced Na^{24} by the deuton bombardment of sodium. Its half-life is 15 hours, and the upper limit of its electron spectrum about 2 m.e.v. It gives off about 1 gamma-ray per disintegration, the energy of the gamma-rays being tentatively given as 5.5 m.e.v.

VII? A 40-second activity found by Fermi (4, 43) in sodium after neutron bombardment is possibly to be attributed to Ne^{23}. (Reference 45.)

VIII A 15-hour half-life for the emission of electrons is found in sodium after neutron bombardment (11, 94) and is due to the same Na^{24} discussed above.

12. Magnesium

I Positrons, known to be emitted from magnesium after bombardment with alpha-particles (26), probably come from Si^{27}. The half-life for positron emission is not known, however (1, 27), because of the fact that the negative electrons emitted are four times as numerous. These come from reaction II. (References 27, 38.)

II Alichanow, Alichanian, and Dzelepow (1) were the first to point out that the measured half-life of about 2.3 minutes for magnesium was that of electron emission. The electrons have a maximum energy of 3 m.e.v. (27, 29), and the radioelement involved is Al^{28}. (Reference 2.)

? Fahlenbrach (41) has found a half-life of 7 or 8 minutes in magnesium bombarded with the alpha-particles of ThC_1, in addition to that of 2.3 minutes mentioned above. This has been confirmed by Eckardt (36). This may be attributed to the positrons from Si^{27} (see above), in which case we have an example of reaction I; alternatively the activity can be attributed to Al^{29} formed in accordance with reaction II, the parent nucleus being Mg^{26}. A determination of the sign of the electrons emitted would serve to decide which is the true reaction.

VI Magnesium, when bombarded with neutrons (4, 43), exhibits a 40-second period which may be tentatively identified with that shown by sodium and attributed to Ne^{23}. (Reference 85.)

VII A 15-hour period observed in magnesium (4, 43) is doubtless to be attributed to Na^{24}.

VIII A weak and water-sensitive period (4, 43) of 10 minutes observed in magnesium is probably that of Mg^{27}.

13. Aluminum

I One of the three elements in which artificial radioactivity was first discovered by Curie and Joliot (26) is aluminum. The positron emission from this element is due to P^{30}, as has been shown chemically (27). The half-life is about 3.3 minutes, and the upper limit of the energy spectrum is 2.74 m.e.v. Ellis and Henderson (38) have studied the yield of this P^{30} as a function of alpha-particle energy, and find a pronounced flattening beyond 8 m.e.v., this corresponding to the height of the potential barrier of the aluminum nucleus for alpha-particles. (References 2, 27, 40, 74, 80.)

IV Lawrence (64, 73) has reported that bombardment of aluminum with high-energy deutons gives a radioactivity with a half-life of 2.5 minutes, which is without question to be attributed to Al^{28}.

VI Under neutron bombardment, Fermi (4, 43) has found a period of 15 hours excited in aluminum. This he showed chemically to be due to an isotope of sodium, so it is clear that we have again to deal with Na^{24}.

VII Another period for electron emission observed in aluminum bombarded with neutrons is a 10-minute one, which Fermi (4, 43) has shown to be due to an isotope of magnesium, necessarily Mg^{27}. (References 45, 57, 76, 85.)

VIII Aluminum bombarded with neutrons exhibits a period of 2.3 minutes (4), which is quite strong when the aluminum is irradiated under water. This is clearly due to Al^{28}.

14. Silicon

II Fahlenbrach (41) has found that an electron-emitting radioelement of about 17 days half-life is formed in the bombardment of silicon with the alpha-particles from a source of ThB + C. An effect of double his background was found after 18 days' bombardment with a source of 6 mc. which was renewed each morning. The radioelement is probably P^{32}, owing to the agreement in half-lives.

VII Silicon bombarded with neutrons has been found by Fermi (4, 43) to have a 2.3-minute beta-activity, which has been chemically demonstrated to be due to Al^{28}. (References 28, 45, 76, 85.)

VIII Under neutron bombardment silicon also exhibits a weak and water-sensitive activity of half-life of several hours. This is probably due, according to Fermi (4), to Si^{31}.

15. Phosphorus

I Frisch (47) has reported positron emission from phosphorus bombarded with alpha-particles. Its half-life is about 40 minutes and the upper limit of the energy spectrum about 1.8 m.e.v. The activity has been shown chemically to be due to an isotope of chlorine, doubtless Cl^{34}.

VI Curie, Joliot, and Preiswerk (28) first noticed a decay period of 2.3 minutes in phosphorus bombarded by neutrons, which Fermi (4) has chemically demonstrated to belong to Al^{28}. (Reference 27.)

VII Fermi (4, 43) showed by chemical tests that a 2.4-hour period found in phosphorus bombarded with neutrons was that of Si^{31}. Half-value thickness of the beta-rays in aluminum is 0.15 g. per square centimeter. (References 28, 61.)

16. Sulfur

VII P^{32}, formed in the bombardment of sulfur with neutrons, has been chemically identified by Fermi (43). It has a half-life of 14 days, and the half-value thickness for absorption of the electrons in aluminum is 0.10 g. per square centimeter. (Reference 6.)

17. Chlorine

VI P^{32} may also be formed by bombardment of chlorine by neutrons. (References 4, 6, 43.)

VIII A water-sensitive period of 35 minutes has been shown by Fermi (4) to be due to a chlorine isotope, either Cl^{36} or Cl^{38}. (Reference 3.)

19. Potassium

I Alpha-particle bombardment of potassium gives a positron emitter of a half-life of 3 hours, which Zyw (98) has demonstrated to be an isotope of scandium, probably Sc^{44}.

VIII An induced activity found by Fermi (4) in potassium irradiated by neutrons is strongly water-sensitive, and chemical tests show it to be an isotope of potassium, probably K^{42}. The half-life is 16 hours.

20. Calcium

I Frisch (27) has reported that Sc^{43}, a positron emitter of 4.4-hour half-life, is formed by bombarding calcium with alpha-particles. Half-value thickness is 0.06 g. per square centimeter of aluminum.

VII Hevesy and Levi (59) report having found and identified chemically a 16-hour activity belonging to K^{42}, produced in calcium by neutron bombardment. Fermi, on the other hand (4), using sources of neutrons twice as strong as that employed by the former investigators, finds no activity.

VIII Hevesy and Levi (59) also report a 4-hour activity due to an isotope of calcium. This was not found by Fermi (4).

21. Scandium

VI Hevesy (58) reports that K^{42} was shown by his chemical tests to be the radioelement of 16-hour period formed by neutron bombardment of scandium. The maximum energy of the beta-rays emitted is given as about 1.2 m.e.v.

22. *Titanium*

? A very weak effect, with a period of a few minutes, was observed by Fermi (43) after neutron bombardment, and may possibly be accounted for by the presence of impurities.

23. *Vanadium*

VIII The half-value period of the activity (43, 4) produced in vanadium by neutron bombardment is 3.75 minutes; the half-value thickness for the beta-rays is 0.17 g. per square centimeter of aluminum. The beta-rays are accompanied by a gamma-radiation. The activation is strongly sensitive to the presence of substances containing hydrogen. The radioelement is V^{52}.

24. *Chromium*

VII The activity (7, 16) induced in chromium by the action of neutrons is also due to V^{52}.

25. *Manganese*

VI V^{52} is also formed by the neutron bombardment of manganese.

VIII A water-sensitive activity of 2.5 hours half-life is formed in manganese by irradiation with neutrons; this can be shown chemically to be due to an isotope of manganese, and it must therefore be Mn^{56}. (References 4, 85.)

26. *Iron*

VII Mn^{56} is formed in the action of neutrons on iron (43, 4). (References 28, 45, 85.)

27. *Cobalt*

VI Cobalt bombarded with neutrons is transformed into Mn^{56}. (References 43, 4.)

VIII Rotblat (88) has reported a weak and water-sensitive activity in cobalt bombarded with neutrons. This is to be attributed to Co^{60}. The fact that cobalt shows a strong absorption for slow neutrons, this absorption being accompanied by the emission of gamma-rays (4), remains unexplained, since the 20-minute activity found by Rotblat seems too weak to account for the observed slow neutron absorption, while the fact that only one stable isotope of cobalt is known makes it unlikely that radiative capture of slow neutrons to form a heavier stable isotope is the process responsible for the absorption.

28. *Nickel*

VII The 20-minute activity due to Co^{60} is reported by Rotblat (88) in nickel bombarded with neutrons.

VIII Rotbalt (88) has also found a water-sensitive activity of a few hours' half-life in nickel bombarded by neutrons. It is likely that it is due to Ni^{63}.

29. *Copper*

IV Lawrence (65) has observed the production of the two radioactive isotopes of copper (Cu^{64}, Cu^{66}) by the bombardment of copper with deutons. This is the heaviest nucleus in which transmutation has been accomplished by means of artificially accelerated particles.[9] The periods are 5 minutes and 10 hours.

VIII Both copper neutron-capture reactions giving rise to the radioelements mentioned above are strongly enhanced by the presence of water. The periods given above are those of Fermi (4); for the long period Bjerge and Westcott (11) report 6 hours. (References 54, 57, 85.)

30. Zinc

VII The long period due to radiocopper (see above) is found in zinc^{59} which has been subjected to neutron bombardment. The active copper has been separated chemically (4) and electrochemically (54). The same remarks apply to the short-period radiocopper. (References 28, 71.)

? McLennan, Grimmett, and Read report a 100-minute period in zinc bombarded with neutrons (70). The origin of this is not known.

31. Gallium

VIII Two half-lives corresponding to neutron capture by the two known isotopes of gallium are observed (4). The stronger is the shorter; its half-life is 20 minutes. Half-value thickness for the beta-rays is 0.17 g. per square centimeter of aluminum. The longer period is 23 hours, and the beta-particles are accompanied by a rather strong gamma-radiation.

32. Germanium

? A very weak activity produced by neutron bombardment of germanium having a half-life of around 2 hours has been reported by Sugden (93). The identity of the radioelement is not known.

33. Arsenic

VIII Neutron capture in this element results in the formation of As^{76}, whose half-life is 26 hours. The beta-particles are half absorbed in 0.16 g. per square centimeter of aluminum (4). (Reference 83.)

34. Selenium

VIII The 35-minute activity (4) produced in this element by irradiation with neutrons has been shown to be due to an isotope of selenium.

35. Bromine

VIII Two neutron-capture reactions have been known for bromine for some time. These lead to Br^{80} and Br^{82}, whose half-lives are 18 minutes and 4.2 hours (4). Half-value thickness for the beta-rays of both radioelements is 0.12 g. per square centimeter of aluminum, and each radioelement emits fairly strong gamma-radiation. (References 3, 14.)

? Recently, Kourtchatow, Kourtchatow, Myssowsky, and Roussinow (62) reported a longer-period activation of bromine by neutron bombardment, which they have shown by chemical tests to be carried by an *isotope of bro-*

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[9] This statement must now be modified. Dr. M. G. White has informed one of us that Professor Lawrence and his coworkers have now observed radioactivity, produced by deuton bombardment according to reaction IV, in elements as heavy as platinum. The energy of the bombarding deutons was about 5 m.e.v.

mine. The half-life is about 36 hours, and the new radiobromine emits very feebly-penetrating beta-particles, together with a strong gamma-radiation. The upper limit of the electron spectrum is 0.6 m.e.v., and the energy of the gamma-radiation is about 0.65 m.e.v. The existence of this radioelement has been checked by Fermi (5), and the fact that only two stable isotopes exist makes the identity of the third type of radiobromine an interesting puzzle. The original discoverers regarded this as a case where the incident neutron, without being captured, expelled another neutron from the nucleus of Br^{79}, so that the radioelement in question is Br^{78}. This seems very unlikely indeed, as all three reactions involving bromine and neutrons go best at small neutron energies, and the likelihood of a very slow neutron expelling another from a nucleus would seem small.

A possibility is that one of the periods of bromine represents that for positron decay, since both of the possible radiobromine isotopes are so located in the periodic table that either the emission of an electron or that of a positron would return them to stable isotopes, of krypton or selenium, respectively.

37. Rubidium

? Fermi (43) has reported a very weak activity with a period of about 20 minutes in rubidium bombarded with neutrons. Its source is unknown.

38. Strontium

Fermi (4) reports finding no activity after strong neutron irradiation.

39. Yttrium

The large absorption reported by Fermi (4) and by Dunning (33) for slow neutrons in yttrium is now attributed by both these workers to the strong likelihood of contamination of the yttrium sample with a small amount of gadolinium. Only weak and doubtful activity has been found in yttrium strongly irradiated with neutrons.

40. Zirconium

VIII Hevesy and Levi (59) report an activity of 40 hours half-life in zirconium bombarded by neutrons. This they attribute to Zr^{91}. Half-value thickness for the beta-particles is 0.13 g. per square centimeter of aluminum.

41. Columbium

? Strong irradiation with neutrons (4) produces only a doubtful activity, probably due to impurities.

42. Molybdenum

? A very weak activity is exhibited after neutron bombardment. There are at least two periods, one of 15 minutes and one longer than a day. The radioelements responsible have not been identified (43). McLennan, Grimmett, and Read (70) give the half-lives as 25 minutes and 36 hours.

43. Masurium

Owing to its rarity, this element has never been tested for artificial radioactivity.

44. Ruthenium

? Kourtchatow, Nemenow, and Selinow (63) report that on bombardment of ruthenium with slow neutrons, they were able to excite activity showing at least four periods of decay, these being 40 seconds, 100 seconds, 11 hours, and 75 hours. The intensities in equilibrium of these activities are respectively 100, 100, 10, and 40. All periods are extremely water-sensitive, the activity of ruthenium irradiated in air not being observable. The identity in intensity of the two short periods suggests that they are products of successive decay, but none of the radioelements concerned has been identified.

45. Rhodium

VIII Rhodium can be strongly activated (4) by bombardment with slow neutrons. It has two periods, of which the shorter, 44 seconds, is water-sensitive and hence is probably that of Rh^{104}. Half-value thickness for the electrons emitted by this radioelement is 0.15 g. per square centimeter of aluminum.

? A longer period of 3.9 minutes (4) is observed (0.10 g. per square centimeter). The shorter period is much the stronger.

46. Palladium

VIII This element displays at least two periods under neutron bombardment. Both are sensitive to water. The half-lives are given as about 15 minutes, and about 12 hours by Fermi (4). McLennan, Grimmett, and Read (70) give 14 hours for the longer period. The radioelements are probably isotopes of palladium, whose mass-numbers are not known because of the existence of several stable isotopes of Pd (30).

47. Silver

VIII Neutron capture in the two known isotopes of this element gives rise to radiosilver isotopes with half-lives of 22 seconds and 2.3 minutes. They are both very sensitive to water. The chemical nature of the longer period has been shown to be that of silver (43). (References 28, 57, 61, 76, 85, 93.)

48. Cadmium

? The great absorption of slow neutrons in cadmium apparently does not correspond to a strong activation. Several weak activities of different periods have been reported by Fermi, but none has been identified (4).

49. Indium

VIII A 13-second period and a 55-minute period in indium irradiated by neutrons are very water-sensitive and doubtless correspond to the disintegration of the radioelements In^{114} and In^{116}. The electrons from the 55-minute isotope are known to be negative. A third activity of about 3.5 hours was discovered by Szilard and Chalmers (95); it is either not sensitive to water or only moderately so. Fermi (4) has performed experiments which seem to indicate that the two shorter periods of indium are due to radioactive isotopes of indium, so that the radioelement responsible for the 3.5-hour period is not known. This is another case in which alternative positron and electron decay might occur in the case of either In^{114} or In^{116}, so far as the positions of stable isotopes are concerned.

50. Tin

Fermi (4) reports that tin strongly bombarded with slow neutrons remained inactive.

51. Antimony

VIII An activity in antimony induced by neutron bombardment and decaying with a period of 2.5 days has been found by Fermi (4). The half-value thickness for the beta-particles is 0.09 g. per square centimeter of aluminum. Chemical tests have shown the activity to be carried by an isotope of antimony.

52. Tellurium

VIII A weak activity in tellurium irradiated with neutrons has a period of 45 minutes and is water-sensitive. It is probably due to an isotope of Te (4).

53. Iodine

VIII I^{128} is almost certainly responsible for the period excited in iodine by neutron bombardment, as numerous chemical tests have shown. The period is given by Fermi as 25 minutes; half-value thickness is 0.11 g. per square centimeter of aluminum. (References 3, 28, 61, 76, 85, 94.)

54. Cesium

? The half-life of a weak activity produced by neutron bombardment of cesium has been given by McLennan, Grimmett, and Read as 75 minutes (71). Fermi (43) indicates that other periods may exist.

56. Barium

? A weak activity found by Fermi in barium after neutron bombardment has a period of 5 minutes and is not water-sensitive. Its identity is not known (43).

VIII A water-sensitive 80-minute period has been shown by chemical tests to be due to an isotope of barium. It is no doubt Ba^{139} formed by neutron capture (4).

57. Lanthanum

VIII Although Fermi has been unable to find any activity in lanthanum irradiated with neutrons (4), Sugden (69) reports an activity of half-life of 1.9 days which is water-sensitive and no doubt belongs to La^{140}. It could have been missed by Fermi because of the brevity of his irradiation.

58. Cerium

Marsh and Sugden (69) and Fermi (4) agree in finding no activity in cerium after neutron bombardment.

59. Praseodymium

VIII Fermi (43), Sugden (69), and Hevesy and Levi (60) agree in finding a 19-hour period which is water-sensitive and doubtless corresponds to neutron capture in praseodymium. Half-value thickness for the beta-rays is 0.12 g. per square centimeter.

? An activity of 5 minutes half-life was early reported by Fermi (43). It is not water-sensitive, and its carrier is not known.

60. Neodymium

? Fermi (43) reports a very weak activity of 1 hour half-life in this element, which was not found by Sugden (69) but was found by Hevesy and Levi (60).

61. Illinium

This element has never been tested for artificial radioactivity.

62. Samarium

? A weak activity with a period of about 40 minutes has been found after neutron bombardment by Fermi (43), and confirmed by Sugden (69), and by Hevesy and Levi (60). In addition, Sugden reports a much longer period. The identity of the radioelement is unknown.

63. Europium

VIII An extremely intense activation apparently due to neutron-capture to form Eu^{152} or Eu^{154}, which has a half-life of 9.2 hours, has been found by Sugden (69, 93) and confirmed by Hevesy and Levi (60). Half-value thickness for the beta-particles is 0.11 g. per square centimeter.

64. Gadolinium

? Although this element absorbs slow neutrons very strongly, only a very weak activity has been found by Fermi (43) and Hevesy and Levi (60). The period was 8 hours. Since Sugden (69, 93) found no activity, the possibility of europium contamination of the former authors' gadolinium samples should be borne in mind.

65. Terbium

VIII The 3.9-hour activity discovered by Sugden (69, 93) and confirmed by Hevesy and Levi (60) is apparently to be attributed to Tb^{160} formed by neutron capture.

66. Dysprosium

VIII The strongest artificial radioactivity found to date in reactions involving neutron bombardment is the 2.5-hour activity of dysprosium. The reaction is strongly water-sensitive, and no doubt is due to Dy^{165}. This radioelement has been investigated by Hevesy and Levi (60) and by Marsh and Sugden (69). Half-value thickness for the emitted electrons is 0.07 g. per square centimeter of aluminum.

67. Holmium

VIII Hevesy and Levi (60) report an activity of 35 hours shown by one of their samples which had undergone neutron bombardment. Since dysprosium is one of the most abundant of the rare earths, and since it shows such an enormous activity under neutron bombardment, one must regard with caution the statement of Marsh and Sugden (69) that carefully purified holmium, free from dysprosium, exhibited a period of 2.6 hours, since it may so readily have been caused by contamination of the holmium with a few hundredths of a milligram of dysprosium. The intensity of the 35-hour period is very high, and the half-value thickness of aluminum for the beta-particles is 0.11 g. per square centimeter. The radioelement is Ho^{166}.

68. Erbium

? Reports on the neutron-produced radioactivity of this element are in conflict. Marsh and Sugden (69) report periods of about 7 minutes and 1.6 days, the latter being about ten times as intense as the former. Hevesy and Levi (60), on the other hand, report a period of 12 hours. Nothing is known about the carriers of the activity.

69. Thulium

Artificial radioactivity has never been sought in this element.

70. Ytterbium

? Marsh and Sugden (69) and Hevesy and Levi (60) are in agreement in finding an activity of 3.5-hours half-life in ytterbium bombarded with neutrons. The identity of the radioelement is not known. The activity is weak.

71. Lutecium

? Here another serious disagreement exists. Hevesy and Levi (60) report an activity induced in lutecium by neutron bombardment whose period is about 5 days. Marsh and Sugden (69) report finding a 4-hour period, and no other.

72. Hafnium

VIII Hevesy and Levi (59) have reported an activity with a half-life of several months to be excited in hafnium by neutron bombardment. This is probably a reaction involving neutron capture, the radioelement being Hf^{181}. This is the longest period reported to date.

73. Tantalum

? Fermi (4) reports having found only a dubious activity after 12 hours' irradiation of tantalum with 500 mc. of radon–beryllium. This is confirmed by McLennan, Grimmett, and Read (70).

74. Tungsten

VIII Fermi (4) found an activity excited in tungsten by neutron bombardment. It is water-sensitive and the carrier of the activity has been chemically shown to be a tungsten isotope. McLennan, Grimmett, and Read (70) give 25 hours for the period.

75. Rhenium

VIII Fermi (4) discovered a water-sensitive activity produced in rhenium by neutron bombardment, and showed chemically that it is borne by an isotope of rhenium. Half-life is 20 hours, and the emitted beta-particles are half absorbed in 0.12 g. per square centimeter of aluminum.

76. Osmium

Fermi (43) found that this element, irradiated 15 hours with 450 mc. of radon–beryllium, was inactive.

77. Iridium

VIII A 19-hour period reported by Fermi (4) in iridium bombarded with neutrons is much enhanced by water, and is probably due to an isotope of iridium. Sosnowski (91), on the other hand, finds periods of 50 minutes and 3 days, the shorter one being accompanied by the emission of gamma-rays.

78. Platinum

? Fermi (4) found a very weak 50-minute activity in platinum bombarded with neutrons. The half-life, according to McLennan, Grimmett, and Read (70), is 36 minutes. Sosnowski (90) reports a half-life of 100 minutes.

79. Gold

VIII Fermi (4) found a water-sensitive period of 2.7 days in gold bombarded by neutrons. The half-value thickness for the beta-rays, which have been shown to be electrons, is 0.04 g. per square centimeter of aluminum. The radioelement is doubtless Au^{198}. Sosnowski (89) has confirmed the half-life and penetration measurements on the electrons emitted, and has claimed to find a gamma-radiation with a half-life of about 5 hours, to which corresponds no known period of beta-decay. This surprising result may be a consequence of the very weak initial intensity of his gamma-rays. (References 76, 85.)

80. Mercury

Fermi (4) has failed ts find any activity after strong irradiation with slow neutrons, in spite of the large absorption (see section VIII) shown by mercury for slow neutrons.

81. Thallium

? McLennan, Grimmett, and Read (71) report an activity with a 97-minute half-life to be produced in the bombardment of thallium with neutrons.

82. Lead

No activity has been found by Fermi (4) after neutron bombardment.

83. Bismuth

? A weak activity of 100-minute period observed by Sosnowski (92) in bismuth bombarded with neutrons must be regarded as doubtful, as it has been denied by Fermi (4), and by McLennan, Grimmett, and Read (71). Bismuth has only one known isotope, Bi^{209}, while Bi^{210} is RaE, a beta-active body of 5 days half-life. The existence of the 100-minute activity in bombarded bismuth was regarded by Sosnowski as being a case of nuclear isomerism.

90. Thorium

Fermi (4) reports periods of 1 minute and 24 minutes in thorium bombarded with neutrons, and states that these activities are "scarcely sensitive to water."

Hahn and Meitner (53) report that the period of 1 minute is not water-sensitive, and that it is the parent of an 11-minute activity. They have further found a period of about 30 minutes, which is water-sensitive, which is identical with Fermi's 24-minute body, and has been chemically shown to be an isotope of thorium. Hahn and Meitner regard the 1-minute body as being a product of reaction VI. The radioelements are then: 1 minute, Ra^{229}; 11 minutes, Ac^{229}; 30 minutes, Th^{233}.

Curie, v. Halban, and Preiswerk (25) report that activities of half-lives of 1 minute, 15 minutes, 25 minutes, and 3.5 hours are produced on neutron bombardment of thorium. The 25-minute activity is due to an isotope of thorium, and its production is enhanced by the presence of paraffin. It is doubtless Th^{233}. The 3.5-hour body is not chemically similar to thorium, polonium, radium, or uranium, but behaves like lanthanum, and is hence probably an isotope of actinium. They agree with Hahn and Meitner that the 1-minute activity is probably due to an isotope of radium. In a later communication, the same authors have chemically shown that the activity of 1-minute period is due to an isotope of radium, and have found an isotope of polonium having a period of 2.5 minutes which they consider to be a decay product of the active isotope whose half-life is 25 minutes. (See also reference 46.)

92. Uranium

Fermi (4) has found periods of activity, induced in uranium by neutrons, of 15 seconds, 40 seconds, 13 minutes, and 100 minutes. The reactions creating all these radioelements, save the one of 40-seconds half-life, seem to be water-sensitive. For the 15-second, 13-minute, and 100-minute activities, the increase in activation produced by irradiation under water instead of in air is the same in each case. This led Fermi to the conclusion that the 40-second period is due to one primary process, while the other three are chain or branching products arising from another primary phenomenon. The identity of the radioelement with the 40-second period is unknown, but the 15-second, 13-minute and the 100-minute products are regarded by Fermi as radioelements of mass-number 239, and charge-number 92, 93, and 94, respectively.

Hahn and Meitner (52) concluded that the 13-minute and 100-minute activity were probably due to elements beyond uranium and different from one another. In a later communication, they reported that the longest-lived activity reported by Fermi was in fact due to a mixture of the two radioelements of periods about 1 hour and 2 to 3 days. All the three radioelements studied by Hahn and Meitner were shown by their chemical tests to have properties different from any of the known elements. The properties one would predict for elements 93 and 94 have been stated by von Grosse (49).

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